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Electrochemistry of Hydrazine-
Hydrazine Azide Mixtures

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FOREWORD

This report was prepared for the Chemical Sciences Directorate, Air Force Office of Scientific Research, United States Air Force, by the United Technologies Research Center, East Hartford, Connecticut under Contract F44620-72-C-0049. The performance period for the technical program was from 1 March 1972 through 30 June 1976. The Principal Investigator was Dr. C. T. Brown and the Project Monitor was Mr. Denton W. Elliott, Deputy Director, Chemical Sciences, Air Force Office of Scientific Research.

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Electrochemistry of Hydrazine-Hydrazine Azide Mixtures

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LIST OF SYMBOLS

Symbol	Definition	Units
A	Electrode area	cm^2
C	Cell constant	cm^{-1}
c^o	Equilibrium Concentration	mole liter^{-1}
c	Concentration	mole liter^{-1}
D	Dielectric constant	-
d	Diffusion coefficient	moles cm^{-2} sec^{-1}
ΔE	Energy of activation	cal mole^{-1}
I_{lim}	Limiting current	milliamps
J	Ionic strength	mole liter^{-1}
K	Equilibrium constant	-
k	Specific conductance	ohm^{-1} cm^{-1}
R	Gas constant	cal $^oK^{-1}$ mole^{-1}
r	Resistance	ohm
T	Temperature	^oK
V+	Number of cations	-
V-	Number of anions	-
Z+	Cation charge	-
Z-	Anion charge	-
α	Degree of dissociation	-
δ	Thickness of diffusion layer	cm
η	Viscosity	dyne-sec cm^{-2}
Λ	Equivalent conductance	ohm^{-1} cm^2
Λo	Equivalent conductance at infinite dilution	ohm^{-1} cm^2
Λ'	Ionic equivalent conductance	ohm^{-1} cm^2
$\lambda+$	Cation mobility	-
$\lambda-$	Anion mobility	-

SECTION I

INTRODUCTION

Investigation of the electrolysis of hydrazine-hydrazine azide monopropellant for small thruster ignition systems (Ref. 1) has indicated that the direct generation of electrical power may be possible from this system. The results of this investigation suggest that the hydrazine-hydrazine azide monopropellant can serve as a conventional monopropellant, as the electrolyte for an electrical power source, and as a pressurization source for fuel tanks by decomposition to hydrogen, nitrogen and ammonia.

The use of hydrazine as a monopropellant for small thruster applications is well known and hydrazine has demonstrated an advantage over other monopropellants in that it represents a good compromise between the requirements of performance and safety. In continuing studies, the performance of hydrazine has been further improved through the use of mixtures of hydrazine and its derivatives including monomethylhydrazine, hydrazine nitrate and more recently hydrazine azide in various proportions. As an additive, hydrazine azide is especially advantageous since it contains only those elements present in hydrazine itself, i.e., hydrogen and nitrogen. In addition it also serves as a freezing-point depressant. Its relative stability in hydrazine mixtures makes it possible to consider concentrations of this additive in excess of the concentrations levels usually considered safe for hydrazine nitrate.

Electrolytic ignition of the azide propellant is possible si⸱ ⸱ hydrazine azide is completely ionized when dissolved in hydrazine forming the azide ion (N_3^-) and the hydrazonium ion $(N_2H_5^+)$. The specific conductivity for a 23 weight percent azide concentration in hydrazine at 25 C is on the order of 10^{-1} ohm^{-1} cm^{-1} as compared to 10^{-4} ohm^{-1} cm^{-1} for propellant grade hydrazine (Ref. 2). The conductivity of this azide mixture is of the same order of magnitude as that of many aqueous electrolytes used in fuel cell and battery applications.

Hydrazine has been used as a fuel in fuel cells employing a separate oxidizer and an aqueous electrolyte (Ref. 3). This configuration requires a fuel which will be easily oxidized at the anode and is relatively inert at the cathode. The latter requirement is difficult to attain since hydrazine spontaneously decomposes on a metal surface to ammonia, nitrogen and hydrogen. This decomposition is a combination of anodic and cathodic processes which results in a mixed potential at the electrodes and represents an inefficiency in the overall process. It is also necessary to provide a separate, gaseous oxidizer.

The use of hydrazine-based propellants for various electrochemical applications has an advantage in that they fall into the class of electrolyte-soluble reactants which are preferable to gaseous fuels since they are easier to transport and store and do not require the use of expensive porous electrodes necessary to maintain a gas-liquid-solid interface. Thus an all-liquid system based on a hydrazine-hydrazine azide electrolyte might result, for example, in a device that would be much simpler than the conventional electrochemical devices. Fuel storage would also be simple since no cryogenic devices would be necessary. (The freezing point of the 23 percent hydrazine azide/77 percent hydrazine mixture is -17.5 C.)

The preparation and the measurement of the properties of hydrazine-hydrazine azide mixtures have been the subjects of work already accomplished at United Technologies Research Center (UTRC) - formerly United Aircraft Research Laboratories - and reported in Ref. 4. This work has been paralleled by investigations into problems associated with storage of monopropellants such as hydrazine and hydrazine azide mixtures (Refs. 5 through 7). It was determined from these investigations that the heterogeneous decomposition of hydrazine-based monopropellants can be described in terms of an electrochemical auto-oxidation reduction mechanism similar to that found in the corrosion of metals when exposed to aqueous electrolytic solutions.

These electrochemical investigations provided the necessary background for the development of an electrolytic ignition system for small thrusters using monopropellants based on hydrazine-hydrazine azide mixtures. In the course of these investigations the electrochemistry of hydrazine-hydrazine azide mixtures was investigated using a variety of electrode materials (Ref. 1). It was determined that the kinetics of the reactions were such that the anodic reaction was enhanced on some materials and the cathodic reaction on others. The proper choice of electrodes resulted in an electrolytic cell with a potential on the order of 0.6 volts.

Theoretical calculations have shown that the electrical potential of a hydrazine-hydrazine azide cell could be as high as three or four volts if discharge of the azide ion (N_3^-) could be realized. Thus an electrochemical device based on hydrazine-hydrazine azide could be the basis of a high energy density "monopropellant fuel cell" in which the azide ion acts as the fuel.

The investigations cited in Ref. 1 indicate that the electrochemical process in hydrazine is due to the presence of water. Electrolysis of both hydrazine and hydrazine-hydrazine azide yield H_2/N_2 ratios of 2/1 rather than the 1/1 ratio expected if $N_2H_4 \cdot HN_3$ (i.e., N_5H_5) were the active electrochemical species.

The purpose of the investigations reported herein was the identification of systems having high cell potentials, similar to those obtained in other non-aqueous media (Ref. 8 through 10), but with solvent properties that permit high solubilities of the reacting species as well as low viscosity and high electrical conductivity. These investigations were initially directed toward determining the nature of the electrochemical process in anhydrous hydrazine and to studying the kinetics of the azide ion on this media. These investigations included the measurement of electrical conductivity as a function of the concentration of the three most common impurities in hydrazine: water, carbon dioxide and aniline. In addition methods for the removal of water and metal impurities from hydrazine were devised in order to determine the effects of those contaminants on the electrochemical processes.

Current-voltage relationships were studied using a variety of solutes including hydrazine azide. These investigations included detailed measurements on the kinetics of the cathode process in hydrazine. The anodic process presented difficulties in that there was no direct evidence of azide ion discharge. As a result the original scope of work was changed to include monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) as solvents in the hope of providing a larger potential range before solvent decomposition takes place. In addition the scope of the electrochemical kinetic studies was changed from investigations of the $N_2H_5^+$ - H_2 (cathodic) and N_3^- - N_2 (anodic) couples to more conventional metal-metal ion couples as sources of electrochemical activity.

The following sections of this report summarize the findings of the studies and suggest possibilities for future research.

SECTION II

RESEARCH ACCOMPLISHMENTS

1. Purification of Hydrazine

In order to properly evaluate the effect of water on hydrazine azide it was first necessary to prepare hydrazine samples that were relatively free of water. Water is one of the major impurities in hydrazine (the others being carbon dioxide and aniline). Metallic impurities are also present as a result of storage in steel drums.

In view of the wide variety of impurities present, two analytical techniques were used to evaluate the purity of hydrazine. Vapor phase chromatography was used for water analysis, and emission spectroscopy for analysis of metallic impurities.

A. Water Analysis - Experimental Procedure

Analysis for water by means of vapor phase chromatography was found to be the most reliable method for water concentrations in the range 0.05 to 2.0 percent. The chromatographic procedure outlined in MIL-P-27402B (Ref. 11) was used employing a dual-column chromatograph constructed at UTRC. Standards were prepared by adding known amounts of water to a hydrazine sample and extrapolating plots of water peak height versus added water to zero percent added water to determine the water content in the original hydrazine sample. Peaks heights were found to correlate with added water to within $\pm$ 2 percent of the absolute value.

B. Hydrazine Purification Procedures

Several procedures for removal of water from hydrazine have been suggested (Refs. 12 & 13). Of these, two methods were chosen. One employed BaO and/or CaH_2 as drying agents and the second employed vacuum distillation. The former method removes only water while the latter removes water and ionic impurities.

All samples for purification were placed in specially cleaned glassware, and all sample transfers were made in a glove box fitted with a vacuum side chamber. Dry purified nitrogen was used as the blanket gas in the glove box; the moisture level was continuously monitored and was maintained in the range of six to ten parts per million. Samples were treated with BaO or CaH_2 in the glove box in 50 ml pyrex glass sample bulbs fitted with teflon stopcocks for venting and O-ring seal removable caps for filling and taking samples.

Ethylene-Propylene O-rings (non-reactive to hydrazine) were employed in all cases. The O-ring seals were also employed on a specially constructed vacuum system so that samples could be transfered from the vacuum system to the glove box in a sealed condition. The vacuum system valves were also teflon. There was no exposure to metals of any type during any of the operations.

Hydrazine azide hydrazinate was prepared by crystallization from concentrated hydrazine-hydrazine azide solutions. The material was recrystallized from methanol and vacuum dried at room temperature. The dried crystals were stored in the glove box. The moisture content of the crystals was checked by adding small amounts of azide to pre-dried hydrazine. The water content remained constant at 0.78 ± 0.02 percent H_2O for azide additions up to 16.4 weight percent, the highest concentration tested for water content.

The dry hydrazine hydrazinate was found to be very stable and showed no evidence of shock sensitivity. This stability confirms the results of Dresser et.al. who first prepared this salt (Ref. 14).

C. Purification Results - Water

The results of water removal procedures on selected samples are summarized in Table I. The stock hydrazine is Mil Spec (propellant grade) which normally has from 0.5 to 1 percent water. This material was subject to repeated exposures to air prior to use. It is evident from the results in Table I that CaH_2 is a much more effective drying agent than BaO. However, contrary to the results reported in Ref. 13, the exposure time necessary to achieve low water levels is considerable for 16 g CaH_2 in 50 ml samples of N_2H_4. It should also be noted that the total time required for "complete" reaction is not a function of the initial water content as is evidenced by the drying time for stock hydrazine (initial water content of approximately 3 percent) and hydrazine sample B. For all practical purposes the residual water content is on the order of 0.05-0.10 percent.

Vacuum distillation of 20 ml samples of hydrazine, a procedure requiring less than 24 hours, results in water contents on the order of 0.15 percent. This latter procedure is probably the most efficient because of the time factor and because it should also reduce the level of ionic impurities in the sample.

During vacuum distillation the first fraction always had the lowest water content. The second fraction had slightly more, provided at least fifteen percent of the sample was left as residue. Otherwise the majority of the distilled water remained in the second fraction.

D. Purification Results - Ionic Impurities

For this program hydrazine samples were available which had been previously analyzed for impurity content. The levels of ionic impurities in the hydrazine samples had been determined by means of emission spectrographic analysis. In most cases metallic impurity levels were considerably less than 0.1 ppm with the exception of levels for sodium and iron. The material designated sample A was selected from the available samples for further studies of purification techniques because it had a high iron and sodium content in addition to a cadmium content higher than all other samples. The results of the analyses for a portion of this material after vacuum distilled hydrazine (Sample A-1 in Table I) are summarized in Table II. The iron and sodium content were reduced in the first fraction of the distillate; however, the second fraction showed a marked increase in ionic impurities and the levels of impurities in the residue were not substantially increased over that in the original sample. The sample was completely distilled and the residue was leached with deionized water for analysis. The majority of the metallic impurities were evidently carried over with the last portion of distillate. These tests were repeated using another portion of Sample A (A-2 in Table I) in which 17 percent of the sample was left undistilled (residue). In this case, the results (also shown in Table II) indicate that the heavy metals (Fe and Ni) were substantially concentrated in the residue. Sodium was also concentrated in the residue but to a lesser extent than the heavy metals.

Emission spectrographic analyses were also made on stock hydrazine samples that had been dried over BaO or CaH_2. In the latter case, the calcium content was 1.0 ppm, whereas the sample dried over BaO contained 60 ppm Ba indicating the drying over BaO introduced a substantially higher impurity level than drying over CaH_2.

As a result of this survey, the electrochemical measurements were carried out using samples dried over CaH_2 and subsequently vacuum distilled. Fraction #1 was used exclusively. This fraction usually constituted 60 percent of the original sample.

2. Electrical Conductivity Measurements

Electrical conductivity experiments were carried out to determine the total ionic nature of hydrazine containing varying amounts of water and other impurities. Measurements were also taken as a function of temperature to determine the energy of activation for ionic migration as a function of the water and impurity concentrations.

A. Experimental Procedure

Electrical conductivity measurements were taken in a cell of Jones design, Ref. 15, constructed to keep filling tubes and electrode leads separated in order to minimize capacitance effects. The electrodes were platinum disks 1.5 cm in diameter and nominally 1.5 cm apart. The cell size was such that cell constants of about 0.5 cm^{-1} would be achieved, where the cell constant is the effective ratio of the electrode spacing to the electrode area.

Cell constants were determined using 0.01 demal KCl solution. All measurements were taken in a large (2 ft x 2 ft x 2 ft) constant temperature bath filled with white technical oil. The mercury thermostating device was capable of maintaining the bath temperature to $\pm$ 0.05 $^{\circ}$C.

The platinum electrodes were not platinized since the rough surface, while minimizing polarization effects, caused slow but appreciable decomposition of the hydrazine. The decomposition resulted in bubble formation on the electrodes yielding high values for cell resistance.

Cells were filled in the glove box using specially dried syringes. All samples were stored in small sample bottles (50 ml capacity) fitted with teflon plugs complete with rubber septum and valve. In this manner samples could be analyzed for water on the chromatograph both prior and subsequent to conductivity measurements without exposure to the atmosphere.

Measurements were taken using an A.C. conductivity bridge based on a commercial impedance comparitor (General Radio Model #1605-AS5). The remainder of the circuitry was designed at UTRC and included a shielded resistance box and capacitors. All resistance measurements were taken at four frequencies of 1, 2, 5 and 20 kilohertz. Capacitance and impedance were balanced separately. Results were plotted as a function of the reciprocal of the square root of frequency and extrapolated to infinite frequency. The resistance at infinite frequency was used in conjunction with the cell constant to calculate the specific conductance according to:

$$k = 1/r \cdot C \tag{1}$$

where k is the specific conductance in ohm^{-1} cm^{-1}, r is the resistance at infinite frequency and C is the cell constant in cm^{-1}.

B. Specific Conductivity as a Function of Impurity Level

The relationship between conductivity and impurity level (including water) was studied using both UTRC stock hydrazine and selected previously analyzed

samples. The results of those measurements are summarized in Table III. The samples were selected to reflect differences in water content and major ionic impurities. The analyses also include qualitative analysis of parameters such as non-volatile liquid residue left after evaporation of hydrazine at 105°C for twenty-four hours and ash (residue after heating to constant weight at 650°C). The ratio of non-volatile residue to ash is a measure of the portion of the total residue that contains decomposible substances. The non-volatile residue on evaporation of hydrazine is primarily an oily substance which has been identified as carbazic acid, a product of hydrazine reaction with carbon dioxide.

The conductivity results can be correlated with the levels of non-volatile residue and with the ratio of non-volatile residue to ash. For the samples listed in Table III, there does not appear to be any correlation with water content, or the amount of metallic impurities present. It is possible that the non-volatile residue is associated with the formation of complexes of carbon dioxide and aniline, two of the major impurities in hydrazine.

In view of the conductivity results and the fact that metallic impurities are carried over in the distillate when hydrazine is vacuum distilled (see preceding section) it appears likely that "stable complexes" (possibly based on carbazic acid) are formed that are ionic in nature and have relatively high boiling points compared to hydrazine. The presence of these "complexes" make correlation of conductivity with water content extremely difficult.

C. Specific Conductivity as a Function of Temperature

In view of the preceding results the conductivities of selected samples were measured as a function of temperature in order to determine if the level of non-volatile residue results in a different mechanism of ionic migration. Samples A and B (see Table I) were selected for study as was a portion of Sample B which had been dried over CaH_2 for 384 hours. None of these samples had been treated in any other manner. The data were calculated using the Arrhenius type relationship:

$$k = Ae^{-\Delta E/RT} \qquad (2)$$

where k is the specific conductivity in $ohm^{-1} cm^{-1}$, ΔE is the energy of activation for ionic migration in calories/mole, R is the gas constant in calories/°K/mole, and T is the absolute temperature in degrees Kelvin. Plots of log k versus 1/T yield a straight line with a slope of $-\Delta E/R$.

The data for the three samples cited above are summarized in Table IV. The plots obeyed the Arrhenius relationship in all cases.

The energies of activation in Kcal/mole were 2.21, 2.38 and 1.56 for Samples A, B and B dried over CaH_2 for 384 hours respectively. Samples A and B contained 1.20 and 1.47 percent water respectively, and B dried over CaH_2 contained 0.13 percent water. These results indicate that the lowered water content results in less energy necessary for ionic movement in the system. The presence of water evidently has a marked effect on the structure of the liquid. When these results are compared to earlier conductivity studies (Refs. 1 & 2) it is seen that the ease of ionic migration is similar to that achieved when hydrazine azide or hydrazine nitrate (both highly ionic species) are added to hydrazine. For example, the energy of activation for a 77 percent hydrazine - 23 percent hydrazine azide mix (specific conductivity = 1.78×10^{-1} ohm^{-1} cm^{-1} at 25°C) is 1.28 Kcal/mole.

It must be concluded that even though impurities related to the non-volatile residue parameter have marked effect on the specific conductivity, the mechanism of ionic migration is a strong function of water content, and thus water-solvent or water-complex interactions must play a large role in the nature of the liquid structure.

D. Specific Conductivity as a Function of Water Content

Because of the preceding results, experiments were carried out to determine the effect of water on the conductivity of hydrazine using Sample B dried over CaH_2 for 284 hours and having a water content of 0.13 percent after drying. Additions of water were made using sample weight and water weight to calculate water concentration in moles/liter of solution. The density of hydrazine at 25°C (1.004 g/ml) was used as the basis for these calculations. The maximum water content was 28.44 mg in 7.0038 g of solution or 0.406 percent.

Equivalent conductivities were calculated using the equation

$$\Lambda = \frac{k \times 1000}{\text{Conc. } H_2O} \tag{3}$$

where Λ is the equivalent conductivity in ohm^{-1} cm^2, k is the specific conductivity in ohm^{-1} cm^{-1} and the concentration of water is expressed in moles/liter. The data obtained in these experiments are summarized in Table V.

The equivalent conductivity was plotted as a function of the square root of water concentration according to the Onsager relationship which takes the form:

$$\Lambda = \Lambda_o - (A + B\Lambda_o) \sqrt{c} \tag{4}$$

if the water is completely ionized. In Eq. (4) Λ_o is the equivalent conductivity at infinite dilution, A and B are constants which are functions of the solvent (hydrazine) only and c is the water concentration in moles/liter.

The Constants A and B are expressed as:

$$A = \frac{82.4}{\eta \, (DT)^{1/2}} \tag{5}$$

$$B = \frac{8.20 \times 10^5}{(DT)^{3/2}} \tag{6}$$

where D is the dielectric constant for hydrazine which has a value of 51.7, T is the temperature in $^\circ K$ and η the viscosity of hydrazine which has a value of 9.049×10^{-3} dyne-sec/cm^2. Using this data and a temperature of 298°K, A = 73.54 and B = 0.4288. The values used in the numerator of the expressions for A and B are derived from calculated electrophoretic and relaxation forces for an ion surrounded by solvent molecules, and are valid only when assuming a 1:1 electrolyte, i.e., univalent cations and anions. The latter assumption should be valid for this system since it is highly probably that the ions formed are $N_2H_5^+$ and OH^-, as a result of reaction of water with hydrazine.

A plot of $\sqrt{c}$ versus Λ will have an intercept equivalent to Λ_o at c = 0 and a slope of $-(A + B\Lambda_o)$. The value of the slope can be calculated from the known values of A and B and the intercept value of Λ_o. This calculated value of the slope can then be compared with the slope as measured from the plot. The data for Sample B yielded a value for Λ_o of 0.476 ohm^{-1} cm^2 at infinite dilution (the intercept value). The slope of the plot was -0.606 as compared to the calculated slope of -73.74. This large difference in values for the slopes - a factor of approximately one hundred-indicates that the assumption that all the water is converted into ions is not valid. Consequently, the Onsager relationship was modified as indicated in the following paragraph.

Since the hydrolysis of hydrazine

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^- \tag{7}$$
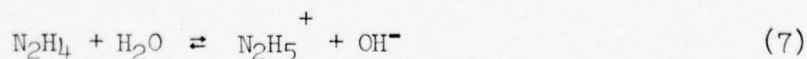
has an equilibrium constant of approximately 8.5×10^{-7} (Ref. 12), it should be possible to replot the data using:

$$\Lambda' = \frac{\Lambda}{\alpha} \tag{8}$$

and

$$\Lambda' \equiv \Lambda_o - (A + B\Lambda_o) \sqrt{\alpha c} \tag{9}$$

where α, the degree of ionization, is calculated from the expression:

$$K = \frac{(N_2H_5^+)(OH^-)}{(H_2O)} \ . \tag{10}$$

Since N_2H_4 is present in excess, its concentration is assumed to be constant. For univalent cations and anions,

$$X = (N_2H_5^+) = (OH^-) \tag{11}$$

and thus:

$$K = \frac{X^2}{c-X} \tag{12}$$

or in terms of α:

$$K = \frac{c \ \alpha^2}{1-\alpha} \ . \tag{13}$$

In Eqs. (12) and (13), X is the ionic concentration in moles/liter and c is the original water concentration. Calculating α using Eq. (13) it is then possible to calculate Λ', the ionic equivalent conductance.

The results of these calculations are also summarized in Table V. The data indicates ionic equivalent conductivities on the order of 92 ohm^{-1} cm^2 which are similar in magnitude to equivalent conductivities for ionized species.

Using the values for Λ' and plotting Λ' vs $\sqrt{\alpha c}$ a slope of -72.70 is obtained compared to the theoretical value of -73.74. Thus, at very low water concentrations the Onsager relationship is confirmed provided the hydrolysis reaction is taken into consideration.

Subsequent experiments at higher water concentrations resulted in irregular changes in specific conductivity. The range of water content was from about 0.8 percent to 1.2 percent in one case and 0.8 percent to 2.1 percent in another case. It was found that at concentrations approaching 1.2 percent water the conductivity reached a constant value which was maintained

up to at least 2.1 percent water. These results explain why the samples ana-
lyzed for water as a function of impurity content (Table II) do not correlate
well with the specific conductivities. The water contents in the original
samples tested were at least 0.5 to 1.0 percent water and approached the point
where association took place and the ionic species formed by hydrolysis of
hydrazine were not as readily formed.

E. The Conductivity of the Systems: Aniline-Hydrazine and
Carbon Dioxide-Hydrazine

The results of the conductivity measurements of the aniline-hydrazine
system are summarized in Table VI. The change in specific conductivity with
concentration of aniline was so small that no significance could be attributed
to the measured changes. Since the concentration of aniline normally found in
hydrazine is within the concentration range tested, it was concluded that
aniline has no effect on the ionic nature of hydrazine.

The results of the conductivity measurements for the carbon dioxide-
hydrazine system are summarized in Table VII. These results indicate a large
change in conductivity over a concentration range from about 8×10^{-4} to
3×10^{-2} moles/liter. The specific conductivity ranged from 1.35×10^{-4} to
2.88×10^{-3} ohm^{-1} cm^{-1}. There was some scatter in the data due to difficulties
in introducing gaseous CO_2 into the hydrazine. (Introduction of CO_2 was
accomplished by means of a gas-tight syringe.) Concentrations were based on
weight gain rather than CO_2 volume. In general, the data can be expressed by
an equation having the form of the Onsager equation: (see Eqs. (4) through (6)).

In the water-hydrazine system discussed previously, an alternative form
of the Onsager equation (Eq. (9)) was used since the slope of the Onsager plot
calculated from known values of A and B and the measured intercept was much
greater than the measured slope. When the degree of dissociation (α) was taken
into account for the hydrazine hydrolysis reaction the experimental data
agreed with the calculated Onsager slope for a uni-uni valent electrolyte such
as that indicated in Eq. (7).

The situation with CO_2 is just the opposite of that noted for water.
For CO_2 in hydrazine the calculated slope is -132.84, using an extrapolated
value for Λ_o of 138.2 ohm^{-1} cm^2, while the experimental slope is -309.1 when
the data are plotted in the form of Eq. (9). This larger experimental slope
indicates that the forms of the constants A and B given by Eq. (5) and (6)
could be incorrect since they were derived assuming that the electrolyte is
uni-uni valent. The generalized form for the constants A and B are:

$$A = \frac{29.15(Z_+ + Z_-)}{\eta \, (DT)^{1/2}} \, \sqrt{Z_+ + Z_-} \qquad (14)$$

$$B = \frac{9.90 \times 10^6}{(DT)^{3/2}} \, W \, \sqrt{Z_+ + Z_-} \qquad (15)$$

where Z_+ and Z_- are the charges on the cation and anion respectively and W is defined as:

$$W = Z_+ Z_- \, \frac{2q}{1 + q^{1/2}} \qquad (16)$$

and q is:

$$q \equiv \frac{Z_+ Z_-}{(Z_+) + (Z_-)} \cdot \frac{(\lambda_+) + (\lambda_-)}{(Z_+ \lambda_-) + (Z_- \lambda_+)} \qquad (17)$$

Equation 17 takes into account the effects of the ionic atmosphere (i.e., the ion plus its solvent sheath) and the time of relaxation of the ionic atmosphere when the ion is exposed to an electric field. λ_+ and λ_- are the individual mobilities of the cation and anion, respectively. Usually these values are not known. However, for a binary electrolyte, i.e., one yielding only two ions, Z_+ and Z_- are equal and q is 0.5. For an electrolyte yielding three ions, i.e., one with a charge of -2 and two with charges of +1 each (or vice versa) estimates must be made for λ_+ and λ_- in order to evaluate q. For instance, if λ_+ and λ_- are assumed to be equal, then for a uni-bi valent electrolyte q has a value of 0.266 and W has a value of 0.704. The corresponding values for W are 0.585 and 1.170 for a uni-uni and bi-bi valent electrolyte, respectively.

Using the correct values for Z_+ and Z_- and W in each case, the constants A and B are as follows:

Electrolyte Type	A	B
Uni-uni valent	73.54	0.4288
Bi-bi valent	232.8	0.9940
Uni-bi valent	151.4	0.6360

Since concentrations must be expressed in terms of the number of ions produced per mole of solute, equivalents per liter must be used rather than moles per liter for the concentration term. Thus the concentration term depends on the product formed when CO_2 reacts with hydrazine.

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The behavior of carbon dioxide in the presence of hydrazine is the subject of some controversy. Two reactions may occur. One is based on the formation of carbazic acid, i.e.,

$$CO_2 + N_2H_4 \rightleftharpoons N_2H_3COOH \tag{18}$$

followed by:

$$N_2H_3COOH \rightleftharpoons N_2H_3COO^- + H^+ \tag{19}$$
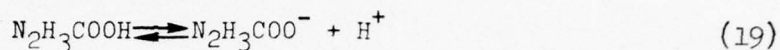
or it is also possible that hydrazinium carbonate is formed, i.e.,

$$N_2H_4 + N_2H_5OH + CO_2 \rightleftharpoons (N_2H_5)_2CO_3 \tag{20}$$

followed by:

$$(N_2H_5)_2CO_3 \rightleftharpoons 2N_2H_5^+ + (CO_3)^{-2} . \tag{21}$$
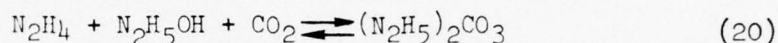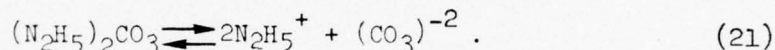
If reactions (18) and (19) take place, then the electrolyte is uni-uni valent and the theoretical slope of -132.84 should be observed. If reactions (20) and (21) take place, three ions will be formed per mole of CO_2 in solution. In order to test the data using the constants noted above, it is also necessary to use the proper concentration terms for the calculation of the equivalent conductivity (Λ) and for the concentration term in the Onsager equation itself. This equation takes the form:

$$\Lambda = \Lambda_o - (A + B\Lambda_o) \sqrt{J} \tag{22}$$

where J is the ionic strength of the solution (assuming complete ionization) and is defined as:

$$J = 1/2 \, c_i Z_i^2 = 1/2 \, (c_+ Z_+^2 + c_- Z_-^2) . \tag{23}$$

In Eq. (23) c_i is the molar ionic concentration and Z_i is the ionic charge. For a uni-uni valent electrolyte the ionic strength is identical to the molar concentration.

The equivalent conductance is calculated using the equation:

$$\Lambda = \frac{k(1000)}{cn_e} \tag{24}$$

where n_e is defined as:

$$n_e = (V_+ Z_+) = (V_- Z_-) \tag{25}$$

and c is in moles/liter and V_+ or V_- are the number of ions of each type formed and Z_+ or Z_- are the charges on those ions. The value of n_e is 2 for either a uni-bi or bi-bi electrolyte, so the calculated equivalent conductivities for both electrolyte types will be one half those calculated from the data summarized in Table VII. The ionic strengths used for the bi-bi and uni-bi electrolyte types are four and three times the molar concentrations, respectively. This data is summarized in Table VIII. Plots of the equivalent conductivity data versus the square root of the ionic strength yield slopes of -75 and -89 for the bi-bi and uni-bi electrolyte types, respectively. The corresponding theoretical slopes are -307 and -208 for the bi-bi and uni-bi electrolyte types, respectively.

The above data analysis indicates the formation of a uni-bi electrolyte since the calculated slope for this electrolyte type is in closer agreement with experimental data than are the calculated slopes for the other electrolyte types. However, if the above conclusion is valid, then the electrolyte formed is not completely dissociated since the experimental slope is about one-half the theoretical slope. If hydrazinium carbonate is formed, it would be necessary to evaluate its degree of dissociation by some independent means in order to evaluate its behavior in a manner similar to that already accomplished in the case of water.

3. Electrode Polarization Studies on Platinum in N_2H_4 Solutions

The polarization of a platinum electrode in various hydrazine-water and hydrazine-hydrazine azide solutions was examined to determine if the cell current could be significantly reduced by removing water. The experiments were also designed to determine what effect water and azide ion would have on the nature of both the anodic and cathodic processes.

A. Experimental Procedures

Polarization measurements were performed using potentiostatically controlled linear voltage sweeps. The polarization cell was designed to keep the contents under a blanket of dry nitrogen at all times. Three electrodes were employed; a platinum counter electrode, a platinum working electrode

(surface area 1.440 cm^2) which was fastened to a rotating device, and a graphite indicator electrode connected to the cell through a Luggen probe. The latter electrode has been shown to maintain a constant, but unknown potential in hydrazine and was selected because at this point in the experimental program a non-aqueous reference electrode had not been developed for this work.

Polarization measurements were carried out in hydrazine solution B (described previously) that had been deliberately contaminated with water to a level of 1.43 percent. Experiments were also performed in solutions dried over calcium hydride (water content 0.05 percent). Metallic contaminants (304SS) and hydrazine azide were added to this base solution to determine their effects on the electrode processes. In order to facilitate comparison of the results as a function of the above parameters, the anodic and cathodic processes are discussed separately. Effects of the anodic process on the cathodic process and vice-versa are discussed in a separate section.

B. Anodic Polarization Results

The shapes of the anodic current-voltage curves were almost identical in all cases. There appeared to be almost a linear relationship between these two parameters. The only difference noted in the absence of hydrazine azide was the current level, achieved as a function of applied overpotential (Table IX). Voltage scan rates were also varied during these runs from 0.2 volt/sec to 6 volts/sec. There was no difference in the anodic current achieved over this range. Electrode rotation speeds in the range 200-1000 rpm resulted in a slight decrease in the maximum anodic current indicating a small reverse diffusion effect that may be due to film formation that inhibits the removal of an anodic product.

In the highly purified N_2H_4 (0.05 percent H_2O) a maximum current was reached after several anodic runs. As the number of runs increased the voltage at which this maximum current was achieved decreased from an applied anodic polarization of +2.4 volts to a limiting value of +1.0 volt. This maximum current did not behave in the same fashion as one would expect from a limiting current, but appeared to be more consistent with the film formation on the electrode surface as noted above. The effect could be reversed, so that the electrode returned to its original condition, by cathodic polarization, electrode rotation or by simply allowing the system to come to equilibrium. This effect is illustrated in the sequence in Fig. 1. The surface species is evidently highly resistant in nature, but is not strongly adsorbed on the electrode surface, and only appears when the water content is low and polarization is extended to greater than 2.0 volts. It can also be noted in

Fig. 1D that this maximum current is not achieved when electrode rotation is employed. This "adsorbed film" is evidently not formed in significant quantity at the electrode under forced flow conditions.

The effect of the addition of a small amount of hydrazine azide is quite evident from the data in Table IX. An anodic current of 60 ma is achieved at an anodic overpotential of 1.0 volt, which is at least an order of magnitude greater than hydrazine or hydrazine containing metal ions. The effect of electrode rotation is still the same, as can be seen in Fig. 2, where polarization is illustrated at a maximum polarization of +0.40 volt.

Aside from the large increase in current, it is not immediately apparent that the anodic process is different from the process taking place in purified hydrazine. The effect of rotation is still the same, and the presence of the resistive intermediate cannot be determined since it was not possible to polarize to the 2.0 volt level due to the very large currents obtained.

In addition to the above experiments, anodic polarization was also investigated using hydrazine A (0.51 percent H_2O) and hydrazine B (0.13 percent H_2O). These solvents were used in conjunction with potassium chloride as well as hydrazine azide and hydrazine hydrochloride.

The results of anodic polarization on platinum as a function of electrolyte composition for the solutes specified above are illustrated in Fig. 3. The current densities achieved at a constant overpotential of 0.8 volt are summarized in Table X. The addition of potassium chloride to hydrazine A at 0.8 volt overpotential results in a current density of 35.5 milliamps/cm^2, which is considerably above the results for all the rest of the solutions studied and is probably due to a combination of increased conductivity and the amount of water present. The fact that hydrazine A has a slightly higher current density at a given overpotential than hydrazine B is not surprising in view of the additional water in hydrazine A. Hydrazine B containing potassium chloride, hydrazine azide or hydrazine hydrochloride all exhibit almost identical behavior which leads to the conclusion that there is simply one anodic reaction for all three of these systems, only one of which contains the azide ion. Therefore, it appears that the azide ion is not discharged and that the reaction taking place at the anode is simply the reaction of hydrazine molecules to form nitrogen. Since the water concentration for hydrazine B is only 0.13 percent, and the results for the anodic process is very similar to previous results at 0.05 percent water, it appears that water concentrations in this range have no effect on the anodic electrochemical processes in the hydrazine solutions.

C. Cathodic Polarization Results (Solutes H_2O and N_5H_5)

Cathodic polarization in hydrazine resulted in a reduction wave at high water content and when the solution contained metallic contaminants. In purified hydrazine this wave was almost nonexistent (<1.0 ma peak current) and was not evident in azide solution. Figure 4 shows the cathodic current-voltage relationships for 1.43 percent H_2O, purified N_2H_4 (0.05 percent H_2O) and hydrazine-hydrazine azide (0.23 percent). In the latter case a limiting current is evident at potentials and current levels considerably greater than the peak currents and potentials in the other electrolytes.

Where a cathodic wave is present, the peak current and peak potential have been found to be functions of sweep rate. Shifts in peak potential indicate an irreversible process. The data for this shift is summarized in Table XI. Thus there exists an irreversible reduction wave which is dependent on water and/or metallic impurities for its presence.

The reduction process in these cases appears to be diffusion controlled since use of the rotating electrode results in the disappearance of the peak and greatly increases the overall cathodic current. However, in the purified hydrazine the effect of rotation is not at all pronounced. The two effects are illustrated in Fig. 5.

The cathodic process in hydrazine azide is definitely diffusion controlled at very high currents and may indeed be the same process as in the contaminated electrolytes. The effect of rotation speed on this process is clearly indicated as shown in Fig. 6. The data for these runs are summarized in Table XII. These limiting currents are greater by a factor of 500 than those achieved at rotation speeds of 90 rpm in purified N_2H_4. The cathodic current at this speed in N_2H_4 with 0.05 percent H_2O was 0.12 ma at -0.8 volt overpotential, and about 10 ma at -1.0 volt in N_2H_4 with 1.43 percent H_2O.

The cathodic process was also studied using hydrazine A (0.51 percent H_2O). This solvent was used in conjunction with the solutes; potassium chloride, hydrazine azide and hydrazine hydrochloride. The investigations were carried out with a stationary electrode and with a rotating electrode.

D. Cathodic Polarization (Stationary Electrode)

Cathodic polarization as a function of electrolyte composition in the absence of electrode rotation is illustrated in Figs. 7 through 11. Figure 7 shows cathodic polarization at a scan rate of 200 millivolts/sec for both hydrazine A and B with and without potassium chloride as a solute. There is

no reduction peak corresponding to the hydrazonium ion in hydrazine B. Hydrazine A on cathodic polarization indicates a distinct reduction peak at an overpotential of -0.7 volt. When KCl is added to these two solvents, the behavior is somewhat changed in that very high cathodic currents are noted at an overpotential of about -0.3 volt (also shown in Fig. 8). When potassium chloride is added to hydrazine B this oxidation peak is not apparent. Figure 8 illustrates the case of hydrazine A with potassium chloride for a first cathodic scan and on a 6th successive cathodic scan. As additional cathodic scans are made, the hydrazonium ion reduction peak diminishes and the oxidation peak appears. It also has been determined that if the polarization is not carried out past -0.8 volt, where large currents are seen, then the anodic peak is not present. When the same procedure is carried out in hydrazine B containing potassium chloride, as illustrated in Fig. 9, the reduction peak at -0.3 volt disappears on successive scans but the oxidation peak apparently shifts potential to a very low over-voltage. It is difficult to determine if this "peak" corresponds to a true oxidation. In any event for hydrazine A, the oxidation peak and the reduction peak are both at -0.3 volt and the phenomena must have something to do with the presence of water. In both cases potassium chloride is simply acting as a supporting electrolyte so that the processes that are going on more nearly indicate a true diffusion process, whereas in hydrazine without any supporting electrolyte any limiting current phenomena is due not only to diffusion but also to migration because of the potential gradient in the system. In the case of hydrazine A as shown in Fig. 8, it appears that at least part of the reduction product remains on the surface and is reoxidized regardless of which reaction is taking place due to hydrazonium ion reduction. It has also been established that constant gas evolution does not occur until the cathodic overpotential is greater than -0.8 volt although some gas bubbles are formed on the electrode at -0.3 volt.

The irreversibility of the cathodic process is illustrated in Fig. 10 where cathodic polarization on hydrazine A was carried out at three different scan rates; 200 millivolts/sec, 20 millivolts/sec, and 6.7 millivolts/sec. At the fastest scan rate the overpotential for the reduction peak is -0.7 volt. At lower scan rates the peak potential shifts in the positive direction so that at the lowest scan rate of 6.7 millivolts/sec the peak potential is on the order of -0.5 volt. This shift in potential for an electron transfer process is indicative of an irreversible system. In the case of a completely reversible system the potential should be independent of scan rate.

Figure 11 illustrates the cathodic polarization in a stagnant solution (stationary electrode) in the case where hydrazine azide and hydrazine hydrochloride were added to hydrazine B. The result is σ quasi-limiting current, no hydrazonium ion reduction peak, and a potential of -1.0 volt at which this quasi-limiting current begins. The half-wave potential of this process is about -0.8 volt and corresponds to the onset of hydrogen evolution noted in the N_2H_4/KCl solutions. This potential seems to be independent of the electrolyte composition while the hydrazonium ion reduction peak does not.

E. Cathodic Polarization (Rotating Electrode)

For each of the two hydrazine solvents and for the three solutes investigated, a large number of experiments were carried out using a rotating platinum electrode to determine the nature of the diffusion characteristics of the hydrazonium ion both in the presence and the absence of supporting electrolytes. The rotation data for all the experiments is summarized in Table XII. The cathodic behavior on rotation for hydrazine as a function of H_2O and KCl content is illustrated in Figs. 12 and 13 at a rotation rate of about 320 rpm. Using hydrazine A a limiting current of -0.4 milliamps/cm², starting at an overpotential of about -0.4 volt, is noted (Fig. 12). When potassium chloride was added to this system only a quasi-limiting current was noted at this rotation rate. However, at higher rotation rates the limiting current was more pronounced. Apparently more than one electrochemical process is involved in N_2H_4-A/KCl system. As the rotation rate was increased (not illustrated), the potential at which the limiting current was noted also increased in the cathodic direction. Figure 13 illustrates the same effect for limiting currents with potassium chloride added to hydrazine B. In this case, there is very little shift in the potential at which the limiting current is reached but the value of the limiting current is increased. For hydrazine B containing hydrazine azide or hydrazine hydrochloride, (Fig. 14) limiting currents were also noted at very high values on the order of 36 to 40 milliamps/cm². The limiting current densities are at least 2 orders of magnitude greater than those for potassium chloride in hydrazine B.

Using the data in Table XIII and making assumptions about the nature of the diffusion layer in hydrazine, it is possible to calculate a diffusion coefficient for hydrazonium ion using the basic Nernst equation:

$$I_{\ell im} = \frac{z_i \; FdAc^°}{\delta} \tag{26}$$

where $I_{\ell im}$ is the limiting current in milliamps, z_i is the charge on the ion, d is the diffusion coefficient in moles cm⁻² sec⁻¹, A is the electrode area in cm², c° is the equilibrium concentration of the reacting ion in moles-

liter^{-1}, δ is the thickness of the stagnant diffusion layer in cm and F is the Faraday in ampere-sec. This equation can be used for hydrazine azide or hydrazine hydrochloride as solutes since the concentration of the $N_2H_5^+$ ion (C°) is known. The area of the electrode is also known; and, of course, the limiting currents have been measured. The two remaining variables in the equation are the diffusion coefficient for the hydrazonium ion and the thickness of the diffusion layer (δ). According to Kortum (Ref. 16), in aqueous solutions the average thickness of the Nernst diffusion layer in a violently agitated solution is on the order of 10^{-3} cm. Using the highest rotation rates achieved in these experiments and a first approximation that the thickness of the diffusion layer is 10^{-3} cm, then a diffusion coefficient can be calculated. Once the value for the diffusion coefficient has been calculated then it is possible to calculate the concentrations of hydrazonium ion present in solutions containing water or KCL. If these concentrations can be correlated with the calculated values based on the hydrolysis of hydrazine by water within a reasonable variation, then the diffusion control must be due to the hydrazonium ion. The values used in Eq. 26 are as follows: the ionic charge z_i is 1 for $N_2H_5^+$. The concentration of hydrazonium ion is 3.62×10^{-2} moles/liter for hydrazine azide and 3.38×10^{-2} moles/liter for hydrazine hydrochloride assuming complete ionization of the added solutes. The area of the electrode is 1.44 cm^2 and F is the value of the Faraday which is 96,500 amp/sec. The values of limiting current of 84 milliamps/cm^2 for hydrazine azide and 70 milliamps/cm^2 for hydrazine hydrochloride were used for these calculations since they are the highest limiting currents obtained at the highest rotation rates tried in these solutions. The value calculated for the diffusion coefficient for the hydrazonium ion in the hydrazine azide solution is 1.67×10^{-5} moles cm^{-2} sec^{-1} and for the hydrazine hydrochloride solution is 1.49×10^{-5} moles cm^{-2} sec^{-1}. The average of these values is $1.58 \pm 0.09 \times 10^{-5}$ moles cm^{-2} sec^{-1} or a deviation of about 6 percent. This value for D was then used to calculate hydrazonium ion concentrations in hydrazine B plus KCl and hydrazine A plus KCl. The value of the thickness, δ, of the Nernst diffusion layer was again assumed to be 10^{-3} cm. The equilibrium concentrations of hydrazonium ion calculated according to the above procedure is 1.00×10^{-3} moles/liter for KCl and hydrazine A and 1.82×10^{-4} moles/liter in hydrazine B containing potassium chloride. The results of these calculations and those based on the hydrolysis reaction (described in the following paragraphs) are summarized in Table XIV.

Hydrazonium ion concentrations were calculated using the hydrolysis reaction written in the form:

$$N_2H_4 + H_2O \;\rightleftarrows\; N_2H_5^+ + OH^- \tag{27}$$
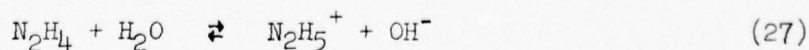
The equilibrium constant for this reaction at 25°C is 8.5×10^{-7}. Using the equilibrium constant expression for reaction (27):

$$K = \frac{(N_2H_5^+)(OH^-)}{(H_2O)} \qquad (28)$$

it is possible to calculate the hydrazonium ion concentration using a quadratic expression:

$$X^2 + KX + C_{H_2O}K = 0 \qquad (29)$$

where X is the concentration of $N_2H_5^+$ and C_{H_2O} is the known water concentration in the electrolyte in question. Using this hydrolysis procedure, the concentration for hydrazonium ion in hydrazine B + KCl is 2.47×10^{-4} moles/liter as compared to a value of 1.82×10^{-4} moles/liter calculated from the diffusion data. The ratio of these concentrations is 1.35 which is considered to be reasonable for this data. When the same calculation is used for hydrazine A containing potassium chloride the equilibrium concentration of hydrazonium ion is 5.30×10^{-4} moles/liter as compared to 1.00×10^{-3} moles/liter from the diffusion data. The discrepancy in the two values for the hydrazonium ion concentration indicates that the apparent concentration of hydrazonium ion as determined by diffusion calculations is very high. In hydrazine A containing potassium chloride plus significant amounts of water, diffusion is not simply a function of the hydrazonium ion but other species such as the hydroxyl ion (OH^-) may be contributing factors. However, the agreement for the hydrazonium ion concentrations calculated from both water analysis and diffusion data in a relatively dry system indicates that the premise of hydrazonium ion diffusion control is correct for systems with low water concentrations. It is apparent that high hydrazonium ion concentrations, as a result of the addition of small amounts of hydrazine azide and/or hydrazine hydrochloride, contribute to rapid diffusion and thus high cathodic currents at low over-potentials.

F. Interrelationships Between Anodic and Cathodic Processes

Anodic-Cathodic polarization curves were run using continuous voltage sweeps, so that each electrode was alternately made the anode and the cathode. The results of such runs in which the electrode was initially the anode are illustrated in Fig. 15 for three cases; purified hydrazine (0.05 percent H_2O) hydrazine contaminated with metallic ions, and hydrazine plus 0.23 percent hydrazine azide. Figures 15A and 15B show the effect in pure hydrazine for initially anodic and initially cathodic cases respectively. The cathode wave is clearly in evidence in the former case indicating that the reduction process is the result of oxidized species placed on the surface during the anodic portion of the sweep. For the initially cathodic case, no such peaks are evident.

Figures 15C and 15D show the same sequence in hydrazine contaminated with metallic impurities. The same general result is evident except that the peaks are much larger in this case, and after several cathodic sweeps (Fig. 15D) the reduction wave is still present.

When hydrazine azide is present the anodic-cathodic sequence of polarization can be reversed with little effect with respect to the total current flow (Figs. 15E and 15F).

G. Discussion and Conclusions

The polarization results indicate that the ion reduced at the cathode is produced during anodic polarization. The only anodic products that could explain the results, with the exception of N_2 (which is an irreversible product) are water and hydrazonium ion ($N_2H_5^+$). The most probable anodic and cathodic reactions are summarized in Fig. 16. The cathodic process has been shown to be diffusion controlled, that is, the diffusing species is directly reduced at the cathode. It has also been shown that the cathodic limiting current is greatly increased by the addition of hydrazine azide at constant water content. Thus the reducible species must be $N_2H_5^+$, and the cathodic reaction proceeds according to one of the following:

$$2 \; N_2H_5^+ + 2e \longrightarrow H_2 + 2 \; N_2H_4$$

$$2 \; N_2H_5^+ + 2e \longrightarrow 2 \; NH_3 + N_2H_4 \qquad (30)$$

$$2 \; N_2H_5^+ + 2e \longrightarrow 2 \; NH_3 + 2 \; H_2 + N_2$$
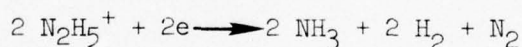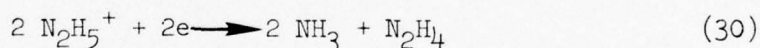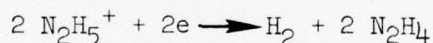
because the $N_2H_5^+$ concentration was increased according to:

$$N_5H_5 \longrightarrow N_2H_5^+ + N_3^- \qquad (31)$$
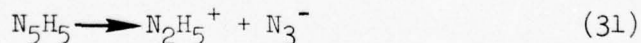
Since the water concentration was not changed when azide was added, the increased cathodic current could not be attributed to the reduction of water to produce hydroxyl ions (OH^-) and hydrogen

The anodic process is limited by electron transfer rather than diffusion and in view of the results of the anode-cathode interaction studies, probably proceeds according to the reaction:

$$5/2 \; N_2H_4 \longrightarrow 1/2 \; N_2 + 2 \; N_2H_5^+ + 2e \qquad (32)$$
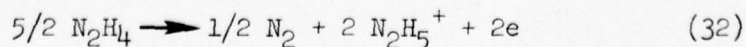
since the reduction of $N_2H_5^+$ is the most probable explanation for the cathodic reduction peak.

It thus follows that adsorption of $N_2H_5^+$ (hydrazonium ion) is the cause of the maximum current in purified hydrazine during anodic polarization (i.e., surface films). The species then desorbs or is reduced cathodically according to reaction (30).

When water is present in significant amounts, $N_2H_5^+$ ions are always present and the cathodic wave is always in evidence (i.e., the reduction of $N_2H_5^+$). The presence of metallic ions may accelerate the self decomposition of hydrazine and thus also contribute to significant amounts of reducible $N_2H_5^+$ ion.

In general it appears that the anodic process is controlled by an electron transfer step involving either hydrazine molecules or azide ions, and the cathodic process is diffusion controlled, the rate being controlled probably by the presence of $N_2H_5^+$ ions.

If the cathodic process is controlled purely by diffusion and not by some preceding or following chemical reaction, then the ratio of the limiting current to the square root of the rotation speed should be a constant (Ref. 17). Calculations using the data shown in Table XII indicate a constant ration for all solutions tested for the cathodic limiting current data in N_2H_4 - 0.23 percent N_5H_5. These results are inconclusive, however the more extensive work, summarized in Tables XIII and XIV indicates that pure diffusion control is present for the cathodic process. Pure diffusion control would eliminate water as the limiting species in the process, since it is only involved as part of a chemical reaction (Fig. 16). The large increase in limiting current upon the addition of azide cannot be interpreted in terms of water since the concentration of the latter was kept constant. The addition of $N_2H_5^+$ would also serve to reduce the effectiveness of water since it reverses the hydrolysis reaction.

Since the cathodic results can be interpreted in terms of $N_2H_5^+$ ion, then the anodic process must also be interpreted in the same manner, and the anodic process is either the direct oxidation of N_2H_4 (reaction 35) or of the azide ion. Confirmation of direct azide ion oxidation was achieved by analysis of gas production at the anode, described in the following section.

4. Electrolysis of Hydrazine-Hydrazine Azide Solutions

Hydrazine samples containing various amount of hydrazine azide and water were electrolized in a two-compartment cell. Each half-cell was connected to a mercury manometer. All volumes were calibrated so that the volume-pressure data could be obtained. Electrolysis was effected by means of an electronic galvanostat and an integrating digital coulometer. The corrected volumes of gas produced, the number of coulombs passed and the gas composition were recorded for each half-cell as a function of time.

If hydrazine is the only electrochemical reactant the reactions:

$$5N_2H_4 \rightleftharpoons N_2 + 4N_2H_5^+ + 4e \tag{33}$$

and

$$4N_2H_5^+ + 4e \rightleftharpoons 2H_2 + 2N_2H_4 \tag{34}$$
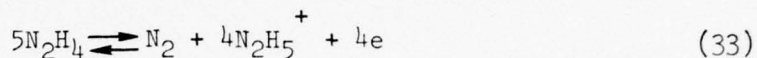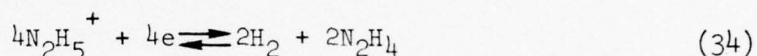
should take place and 0.25 mole N_2 and 0.5 mole H_2 should be formed per Faraday passed. The H_2/N_2 ratio should be 2:1. If the azide ion is electrochemically active, the reactions:

$$2N_3^- \rightleftharpoons 3N_2 + 2e \tag{35}$$

and

$$2N_2H_5^+ + 2e \rightleftharpoons H_2 + 2N_2H_4 \tag{36}$$
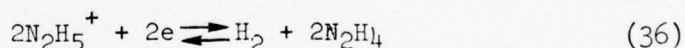
should take place and 1.5 moles N_2 and 0.5 moles H_2 should be formed per Faraday passed and the H_2/N_2 ratio should be 1:3.

Previous electrolysis experiments indicated that the use of platinum electrodes precluded the formation of ammonia in the cathodic process. Gas analysis had also shown that under these conditions the only cathodic product was hydrogen and the only anodic product was nitrogen. In the present experiments, the same results were obtained.

The results of the electrolysis experiments are summarized in Table XIV. Runs 1a and 1b were made using dry purified hydrazine (0.2 percent or 1.11×10^{-1} mole/l H_2O) containing 5.38×10^{-2} moles/l of hydrazine azide. In both cases the mole ratios of H_2/N_2 evolved were initially less than a 2:1 ratio. However, as electrolysis progressed, the mole ratio approached the 2:1 ratio. The moles/coulomb for hydrogen evolution approached the theoretical value in run 1a, but the apparent efficiency for hydrogen evolution was much less than

theoretical during run 1b. During this latter run the efficiencies for both nitrogen and hydrogen evolution were quite low indicating a possible leak in the system.

When water was added to the system (1.11 percent or 0.617 moles/l), the hydrogen evolution efficiency was enhanced (Run #2) as was the efficiency for nitrogen evolution. Again the H_2/N_2 ratio was much less than expected during the early portion of the run.

The hydrazine azide and water concentrations were reduced to 3.72×10^{-2} moles/l and 0.415 moles/l (0.075 percent), respectively (Run #3). The cathode efficiency for hydrogen evolution was very close to theoretical during the entire run, the nitrogen evolution rate was quite large at first and the H_2/N_2 ratio was very close to 1:1.

It appears that the azide ion is preferentially discharged during the early portions of each run. However, there must be a considerable polarization for this reaction and a resulting potential shift to the point where simple hydrazine discharge predominates. In all the runs an increase in cell potential was noted during the runs. This was especially true at the lower azide concentrations. As a result of these experiments, and the electrode polarization studies previously described, it appears that the electrochemical nature of the azide ion in hydrazine is not conducive to the realization of a battery system of high potential. As a result the research was redirected to investigate the nature of electrochemical processes in monomethylhydrazine where large potential ranges can be expected prior to the electrochemical decomposition of the solvent.

5. Electrode Polarization Studies in Monomethylhydrazine

Since there was no direct evidence for azide ion discharge using hydrazine as a solvent, and it has been determined that the presence of water does not hinder the electrochemical reactions in the presence of an ionized solute, the experimental program was redirected in order to investigate substituted-hydrazine materials such as monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH).

The solubility of solute in these solvents is of primary importance since good electrical conductivity is necessary in any system designed for battery applications. The solubility of ionic solutes in MMH is especially important since this solvent is not as polar as hydrazine as evidenced by its lower dielectric constant (Table XV). As shown in Table XVI, the properties of water and hydrazine are very similar. The properties of MMH are somewhat different in that the freezing point and boiling point are lower and the vapor pressure

higher than for either water or hydrazine; nevertheless, these values are still in a range comparable to the other solvents. The only major difference in the properties of these three solvents is the dielectric constant, that of MMH being about one third that of hydrazine. The solubility determinations have shown that in spite of the low dielectric constant the solubilities of hydrazine azide (N_5H_5), sodium azide (NaN_3) and hydrazonium chloride (N_2H_5Cl) in MMH are quite high. The solubility limit of NaN_3 is 0.210 molal (moles/1000 g MMH). The solubility limit of $N_2H_4 \cdot HN_3$ was not reached in these tests but is in excess of 2.39 molal. The maximum concentration of N_2H_5Cl used in these experiments is .097 molal, but judging from the solubility rate, which was quite slow, the solubility limit was being approached. In contrast to the above salts, the limit of solubility of KCl is .007 molal.

Polarization studies were performed using as-received MMH with a specific conductivity of 2.63×10^{-5} ohm^{-1}cm^{-1}. This conductivity is comparable to the lowest conductivities achieved with vacuum distilled hydrazine (1.16×10^{-5} ohm^{-1}cm^{-1}). Most as-received hydrazine has a conductivity of about 10^{-4} ohm^{-1}cm^{-1}. Polarization studies were also performed using as solutes: KCl (.0071 molal), N_5H_5 (.0658 molal) and N_2H_5Cl (.0974 molal). Polarization of MMH as compared to the polarization in hydrazine is illustrated in Fig. 17. In the case of MMH it was possible to polarize out to 3.0 volts in both the cathodic and anodic directions at current densities of less than 0.2 ma/cm^2. It was also observed that rotation of the platinum electrode (0.459 cm^2) up to 1200 rpm had no effect on the current densities achieved.

When KCl was added to MMH (.0071 molal) the current density increased by a factor of 20 in the cathodic direction and the anodic current density increased by a factor of 10. It appears that the majority of the current increase was due to inadequate compensation of IR drop between the reference electrode probe and the working electrode. Thus, the baseline data for solutes with electrochemically active species should be compared with data employing a supporting electrolyte of about the same ionic concentration. The cathodic peak noted in Fig. 17 for MMH plus KCl is probably due to the presence of water in the KCl which results in partial hydrolysis of hydrazine to form hydrazonium ions according to the equation:

$$N_2H_4 + H_2O \rightleftarrows N_2H_5^+ + OH^- \tag{37}$$
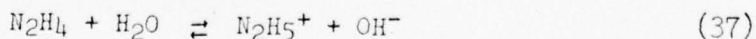
When hydrazine azide (N_5H_5) was added as a solute the current densities were considerably increased. Part of this increase was due to the ionic conductivity because of the higher ionic concentration compared to KCl (0.0658 molal compared to .0071 molal for KCl). The hydrazonium ion ($N_2H_5^+$) does not appear to be diffusion controlled since increased rotation rates of the electrode during cathodic polarization did not affect the current achieved up to a total polarization of 5.0 volts. Thus, it cannot be concluded that any

effects noted with the solutes result in an electrochemically active species that is diffusion controlled even in the cathodic case in the presence of $N_2H_5^+$, though the currents are increased due to added ionic species. The presence of $N_2H_5^+$ does result in gas evolution at a cathodic polarization of about -0.5 volt so that activity achieved must be due to $N_2H_5^+$ ion. However, the process seems to be controlled by electron transfer. In the anodic direction, an overpotential of $+4.0$ volts is necessary before any gas evolution is noted. It is apparent that the azide ion is not active even at those high overpotentials. The results were encouraging in that other anodically active electrochemical species could be chosen that would react without appreciable decomposition of the MMH.

When hydrazonium chloride was used as a solute (.0974 molal) the current densities at equivalent overpotentials were higher in both the anodic and cathodic directions than those experienced with N_5H_5. The larger total current at 3.0 volts anodic overpotential is probably due to increased ionic conductivity in the cell because of the higher concentration. There is no evidence of diffusion control of the $N_2H_4^+$ ion during cathodic sweeps.

With the exception of KCl as a solute the current-voltage relationships are such that there is no evidence of an electrochemically active species other than the $N_2H_5^+$ ion. Even in this case at higher $N_2H_5^+$ concentrations diffusion control is not an important factor. It is apparent that the hydrazonium ion is an electrochemically active species at the cathode, but is not produced at the anode as was the case with hydrazine since anodic-cathodic and cathodic-anodic polarization curves are identical. Thus, the cathodic process in MMH is that of an extremely efficient hydrogen electrode.

A more careful examination of the polarization of platinum in MMH indicates a residual current of 0.22 ma/cm^2 at an overpotential of 1 volt using a bright platinum disk electrode with a surface area of 0.459 cm^2. A Luggen probe with a spacing of 0.1 cm was used. When .007 molal KCl was added as a supporting electrolyte, the residual cathodic current at an overpotential of 1 volt was 0.15 ma/cm^2 at the same probe spacing. Apparently IR drop due to electrolyte resistivity has been virtually eliminated, since the same approximate current density is noted in two solutions of widely differing conductivities. The anodic current density using KCl as a solute in MMH was much larger than in neat MMH. At $\sim$ 1 volt polarization, the current density was 1.5 ma/cm^2.

Examination of the cathodic portion of the current-voltage curves has shown that a small cathodic peak is present at an overpotential of -0.5 volt with a peak current density of 0.17 ma/cm^2. The current at -1.0 volt is somewhat less (as noted above). However, if the cathodic polarization is continued to -1.5 volt,

a rapid increase in current is noted and the current density increases to 1.3 ma/cm^2. A steady evolution of gas is noted at this overpotential. This gas is hydrogen and its formation is apparently due to the reduction of the hydrazonium ion ($N_2H_5^+$), the presence of which is due to the introduction of water associated with the added KCl. Equilibrium polarization studies for both the anodic and cathodic processes have shown that in the cathodic case, gas evolution is achieved at a cathodic overpotential (on platinum) of -0.973 volt and a current density of 0.55 ma/cm^2. In the anodic case, true gas evolution is not achieved at a total anodic overpotential of +1.92 volts (some gas bubbles are noted on the platinum surface however) even though the current density is 11.6 ma/cm^2. The high anodic current density achieved with little evidence of gas evolution suggests a soluble anodic product. It should be noted that the $N_2H_5^+$ ion is probably produced at the anode. However, in the case of hydrazine, this ion was formed along with gaseous nitrogen according to the equation:

$$5/2 \ N_2H_4 \ \rightleftharpoons \ 1/2 \ N_2 + 2 \ N_2H_5^+ + 2e \qquad (38)$$
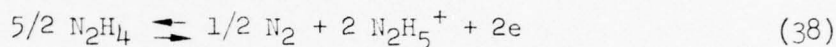
The present polarization studies have shown that a much higher cathodic peak is formed when the electrode is initially polarized anodically and then immediately cathodically polarized. This peak was shown to be due to an increased $N_2H_5^+$ content in the previous studies using hydrazine. Thus, $N_2H_5^+$ is also an anodic product in MMH containing KCl. It has also been established that an anodic peak at zero overpotential is present when the system is initially polarized cathodically beyond -1.00 volt (i.e., hydrogen evolution takes place). This peak is diffusion controlled and must correspond to the oxidation of hydrogen. This oxidation/reduction system is not completely reversible since the oxidation peak is about 0.5 volt anodic with respect to the reduction peak.

The above results (especially for the anodic process) are quite different from those achieved with hydrazine. The reduction peak for hydrazine was only observed during initial sweeps while the oxidation peak was only observed during subsequent sweeps after the reduction peak disappeared. For hydrazine, total surface coverage of a given species must have be to achieved before an oxidation can take place. This surface coverage is apparently not necessary in the case of MMH since both oxidation and reduction peaks are present in the same sweep at all times.

In view of the above results it was concluded that most of the electrochemical reactions in both N_2H_4 and MMH are associated with the solvent itself, even in the presence of ionic species such as the azide ion. The obvious exception is the hydrazonium ion ($N_2N_5^+$) which was added in some cases, but this ion is also present due to water contamination.

Thus it was necessary to examine alternative electrochemical couples that could be used in hydrazine base solvents in order to take advantage of the wide potential operating range afforded by this class of compounds. As a result, candidate metals were studied in hydrazine-family solvents as both soluble anodes and as metal-metal salt couples.

6. Studies Of Candidate Electrode Materials

A series of experiments were performed in hydrazine, monomethylhydrazine (MMH) and in unsymmetrical dimethylhydrazine (UDMH) containing diethylenetetramine (DETA) to determine the electrode potentials of some active metals. The nature of the electrode-electrolyte couple was studied by using separate anode and cathode compartments in the cell and electrolyzing the system in order to generate anodic and cathodic products. The potential decay after termination of the electrolysis was followed until equilibrium was established. In many cases relatively large potential differences were noted after the electrolytic pretreatment. As a result of these studies it was possible to choose for further study several electrode couples which indicated exceptionally large cell potentials.

A. N_2H_4 Containing NaN_3, $NaNO_3$, and a $NaOH-H_2O$ Mixture

The studies in N_2H_4 were designed to determine the current voltage characteristics of the metals aluminum, magnesium, nickel and lead. In addition the reversibility to anode or cathode products were also studied before and after electrolysis by means of potential decay measurements.

The potential measurements obtained before electrolysis reflect the interaction between hydrazine, the inert solute, and the metal. If a relatively high potential is obtained, the reaction of the solution with the metal is usually low. Electrolysis is employed to generate anodic and cathodic products. If these products (ions) are reversible to the metal in question, the potential of the metal should be changed in proportion to the amount of product produced. Thus a large change in potential after electrolysis is desired, and if achieved, suggests that the system should be studied in more detail.

The potential measurements for the three solutes used are summarized in Table XVI. The cases where electrolysis or short circuits were employed are indicated by asterisks. In all other cases only current-voltage sweeps were taken. When electrolysis took place, metal #1 for each couple was the cathode.

When NaN$_3$ was used as a solute, the magnesium potentials versus a platinum reference were always about -1.50 volt regardless of whether electrolysis took place or not. The potentials for lead varied slightly, but were in the range of +0.02 to +0.5 volt. Surprisingly the aluminum potentials were quite variable and ranged from -0.68 to +0.30 volt. In the latter case the aluminum was made the cathode during electrolysis. The nickel electrode potential was only about +0.1 volt. Thus the largest cell potentials involved magnesium because of its high half-cell potential. The largest cell potential was about 1.7 volts for the Mg-Pb couple.

In the presence of NaNO$_3$, the potentials were quite low. The aluminum in this case yielded consistant potentials of about -0.1 to -0.3 volt. After electrolysis however, the potentials increased to about -0.9 volt, indicating the presence of a metal-metal ion or metal-metal salt couple. There was very little change in either the nickel or the lead potentials upon electrolysis and as a result the cell potentials were low. The magnesium potentials were about -0.6 to -0.8 volt.

When a water-sodium hydroxide mixture was used as the solute (i.e., a basic solution the magnesium potentials were about -0.1 volt, however the aluminum potential was about -0.9 to -1.0 volt both before and after electrolysis. In fact, the electrolysis did not produce any drastic changes in the potentials of any of the metals tested indicated that the hydroxyl ion is the primary potential-determining species. Again the nickel potentials were quite low. This metal seems to be the least affected by changes in electrolyte composition since the potentials were about the same in all cases. As was the case for NaNO$_3$, the cell potentials are quite low with a maximum of 1.10 volts for the Al-Ni couple.

The current voltage relationship for the four metals in the three solutes are illustrated in Figs. 18 through 20. The sweep rate was 500 mv/sec in each case. For convenience each metal will be discussed in terms of the three solutes.

Aluminum

In sodium azide (Fig. 18) aluminum is anodically inactive up to an overpotential of about +3 volts. Cathodically the overpotential is about -0.8 volt before a significant cathode current is noted. This corresponds to the beginning of hydrogen evolution. The same anodic behavior is noted for aluminum in sodium nitrate (Fig. 19). However, the cathodic overpotential is about -1.4 volts compared to -0.8 volt in sodium azide. The rest potential is about 0.1 volt compared to -0.8 volt in sodium azide. In sodium

hydroxide solutions (Fig. 20), the rest potential is about -1.1 volt, how-ever, there is little or no cathodic overpotential before there is a signifi-cant cathodic current. The anodic current level is only about 0.14 ma at +5 volts which is considerably less than the other two solutes.

Magnesium

In sodium azide the cathodic behavior is similar to aluminum, the over-potential for hydrogen formation is -0.8 volt. The anodic behavior is such that there is a linear increase in current with overpotential of about 2.5 volts/2 ma. This corresponds to an uncompensated resistance of about 1250 ohms. The anodic reaction is unknown but it could be a combination of nitrogen evolution and magnesium dissolution. The open circuit potential is -1.6 volts versus platinum which is the most negative potential of all the metals studied regardless of the supporting electrolyte.

In sodium nitrate the anodic behavior is considerably different than in sodium azide. There is an overpotential of about +2.6 volts before there is any significant anodic current. However, there is little or no cathodic overpotential and the curve indicates a limiting current.

In the basic solution the equilibrium potential for magnesium is about zero volts compared to -1.6 and -0.8 volts for sodium azide and sodium nitrate, respectively. There is no appreciable anodic current flow up to +3 volts and no appreciable cathodic current flow up to -1.8 volts. The anodic overpoten-tial is about the same for magnesium in $NaNO_3$, but the cathodic overpo-tential is much greater than in all the other experiments.

Nickel

In sodium azide there is minimal overpotential in both the anodic and cathodic directions. There is a slight anodic overpotential of about +1 volt. In sodium nitrate there is an overpotential of ± 1 volt. A cathodic peak is noted at -1.2 volts which corresponds to N_2H_5 discharge. In basic solutions the anodic overpotential is about +1.5 volts, but the cathodic overpotential is practically zero. In all cases the rest potential is practically zero volts. Nickel seems to be the least affected of all the metals tested in terms of both potential and supporting elec-trolyte.

Lead

In sodium azide the open circuit potential is about +4 volts. The anodic sweep is linear and goes through the origin on the return sweep. This linear behavior is also evident in the cathodic direction except that there is a rapid reduction in current from -2.4 to -1.2 ma at -1.5 volts. The cathodic return is also linear but is displaced by -0.9 volts at zero current. This behavior may be due to the reduction of an oxide layer on the lead surface and the -0.9 volt corresponds to lead while the original potential is due to lead oxide. This behavior for both lead and nickel is similar to platinum where an oxidation current is noted at an overpotential of about -0.3 volt provided the cathode polarization is carried out to the hydrogen evolution potential of about -0.8 volt.

In addition to the metal effects it is necessary to consider the general effect of each solute on the behavior of the system. In the case of sodium azide (aside from better current carrying ability) the cathodic currents were greater for aluminum and magnesium than they were for nickel and lead. The anodic curves are similar for magnesium, nickel and lead except that in the latter two cases there is much less uncompensated resistance. Aluminum is the only metal that indicates a large anodic overpotential prior to a significant electrode reaction, i.e., about +4 volts. In all cases it is difficult to ascertain the true behavior of the metal since the primary differences seem to be due to the reaction of hydrazine as a function of the type of metal surface.

In the case of sodium nitrate, the equilibrium potentials are lower than those observed in sodium azide. Also the current voltage relationships are such that the cathodic overpotential is much higher on aluminum than it was in sodium azide. For magnesium there is a much higher anodic overpotential than in sodium azide prior to significant current flow and there is also a cathodic limiting current. In the case of lead there was a much lower cathodic current at a lower overpotential. Thus if the cathodic reaction is to be suppressed, sodium nitrate appears to be a better supporting electrolyte than sodium azide. In basic solution there is a much larger overpotential in both the anodic and cathodic directions for magnesium. The cathodic process seems to be considerably different for in this electrolyte for aluminum, lead and nickel than in sodium azide and sodium nitrate since there is not cathodic peak corresponding to hydrazonium ion discharge.

The overpotentials for each of the metals in the three supporting electrolytes can be used to evaluate their use as possible electrodes. These overpotentials are summarized in Table XVII, and we're obtained by extrapolating the current voltage curves at high overpotentials to the zero current point. It is obvious from the data in Table XVII, that there is no over potential for lead and that the nickel overpotentials are minimal (1.5 to 2.0 volts). However the overpotentials for magnesium increase in the order NaN_3, $NaNO_3$, NaOH (or in the order of increasing alkalinity). Aluminum overpotentials are low in basic solution but there is a wide range of over-voltage for this metal in both NaN_3 and $NaNO_3$.

The usefulness of a given metal as an electrode depends on the desired reactions. Since it appears that the reactions on lead and nickel are due to breakdown of the solvent in the presence of inert supporting electrolytes (it may be that the hydroxide ion is electrochemically active on lead and nickel, but not on aluminum and magnesium) these electrodes should be avoided. When the proper combination of metal and supporting electrolyte are used, the solvent decomposition ceases to be a problem. As a result, the investigation can be extended to a search for metal-metal ion or metal-metal salt couples that can react to provide power without affecting the electrolyte. If these reactions can proceed at low overpotentials it should be possible to realize cell potentials on the order of three to four volts in solutions of high conductivity.

B. Monomethyl and Unsymmetrical Dimethylhydrazine

Because it appeared that hydrazine might be too active electrochemically and the over potentials of the desired electrochemical couples in hydrazine appeared relatively high, tests were undertaken to investigate substituted hydrazines that are much more stable than the parent compound. The use of these compounds as solvents should result in higher overpotentials. especially in the anodic direction. (See Section II-5 of this report for a discussion of monomethlyhydrazine). However the solubilities of ionic compounds are much lower in these solvents than in hydrazine due to their low dielectric constants (see Table XV).

A series of experiments similar to those discussed above were run in MMH. The only solute used was sodium azide (0.085 molar) due to the low solubilities of the other salts in this solvent. The metals, platinum (control) zinc, molybdenum, copper, zirconium and magnesium were used as electrodes. The current levels were low in all cases, but magnesium was the only electrode material that exhibited any appreciable anodic or cathodic overpotential. In the presence of both anodic and cathodic products the

overpotential was about 2.7 volts. Since the current levels are so low (0.02 ma at 3 volts over potential), it is difficult to determine the point at which a significant reaction takes place.

This situation is even more complex in the case of UDMH. It was necessary to add DETA to provide any appreciable salt solubility. It was then possible to dissolve NaN_3 to a 0.17 molar concentration. Aluminum was the only metal tested. It was found that the total overpotential was about 2.2 v in an unelectrolyzed solution. However, this increased to about 6.5 v is a cathodically conditioned electrolyte.

As far as solvent properties go, it may be advantageous to use combinations of N_2H_4 and/or MMH and UDMH to provide the best compromise for solubility and over potential. It is obvious that high anodic over potentials can be achieved in MMH since the anodic process does not involve the production of N_2. Nevertheless, the nature of the anodic process is still not known. However, as noted above, if low over potential electrode couples can be devised which work in hydrazine, then the solubility problems no longer exist.

C. Experiments With Aluminum-Aluminum Salt and Magnesium-Magnesium Salt Couples in Hydrazine

A series of tests were run employing magnesium and aluminum electrodes. Baseline data were obtained for these electrodes by determining current-voltage relationships in the presence of supporting electrolyte only. The supporting electrolyte was 1.7 molar NaCl in most cases. In one case magnesium was tested in the presence of LiN_3. Since sodium salts had been used exclusively in the past, this compound was chosen to see if there was a difference in behavior of the electrolyte if the alkali metal ion was changed.

Once the baseline data were obtained, the salts $AlCl_3 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ were added as solutes. The solubility of these salts were low and the concentration was limited to 0.05 molar in each case.

Aluminum

The aluminum electrode in 1.7 molar NaCl exhibits a high over potential in both the anodic and cathodic directions. The equilibrium potential is about -1.05 volts (Table XVIII) versus a glass reference electrode treated in hydrazine to saturate the glass membrane. This electrode had been found to maintain a steady potential for long periods in compatibility tests run for

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a minimum of one month on another Air Force contract (Ref. 7). The over-
potentials are -1.5 volts cathodic and over +2.0 volts anodic. In the former case
hydrazine evolution occurred with a rapid rise in current at -1.5 volts. In
the latter case no significant current was noted.

In the presence of $AlCl_3 \cdot 6H_2O$ an anodic current was noted at +0.5 volt
followed by a large increase in current at +1.5 volts. The cathodic process
was the same as noted above, i.e., hydrogen evolution at -1.5 volts. The
equilibrium potential changed only slightly -0.670 volt (Table XVIII). The
reaction of aluminum in the presence of an aluminum salt was not very
reversible. There was no evidence of reduction of aluminum ions at low
overpotentials and only a very little oxidation of aluminum at relatively
high anodic overpotentials.

Magnesium

Magnesium in N_2H_4 containing 1.7 molar NaCl indicated a very active
anodic process. The equilibrium potential was -1.34 volts and significant
anodic currents were obtained at an over potential of about +0.8 volt. There
was no evidence of hydrogen evolution or a significant cathodic current out
to -2.0 volts. There was residual current of about 0.5 ma, but this is very low
compared to the usual cathodic currents associated with hydrogen evolution.
There was a double oxidation peak indicating a step-wise oxidation of
magnesium to the +1 and +2 oxidation states.

In the presence of $MgCl_2 \cdot 6H_2O$, the anodic overpotential was reduced
to less than 100 mv and maximum anodic currents (double peaks) were observed
at +0.5 volt. The cathodic overpotential was about -0.35 volt and the cathodic
current was also large. The return cathodic sweep yielded a peak at -0.50 volt
which corresponds to the oxidation of hydrogen. Evidently the reduction of
Mg^{+2} to Mg and the reduction of $N_2H_5^+$ to H_2 occurs at the same potential.
The equilibrium potential is -2.20 volts versus the glass electrode. This
potential is very large and thus the electrochemistry of this couple should
be investigated further. The fact that the $N_2H_5^+$ couple is involved in the
cathodic process is of little concern in this case because the $MgCl_2$ was
added in the hydrated form thus increasing the concentration of the $N_2H_5^+$
ion. This problem can be avoided by adding magnesium in an alternative
ionic form not containing water.

Magnesium was also investigated as an electrode material using LiN_3 as
a supporting electrolyte. The equilibrium potential was -2.08 volts which
is much higher than the potential in any of the other media investigated.
In this electrolyte it was possible to polarize the system to -3 volts without

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appreciable cathodic current. Anodic currents up to 4 ma at +3 volts were obtained, but no evidence of sharp current rises was noted that would correspond to magnesium oxidation.

Experiments using $MgCl_2 \cdot 6H_2O$ in the N_2H_4-LiN_3 system were not successful since the solubility of the magnesium salt was very low in the presence of LiN_3. In this case the concentration of LiN_3 was about 0.26 molar or about five times the concentration used for the other supporting electrolytes. Evidently the total ionic strength was too large for this particular system.

The potentials achieved in these systems are summarized in Table VIII. The magnesium results are encouraging and should be pursued. The results indicate that metal-metal salt couples can be used in hydrazine, provided the proper supporting electrolyte is used.

SECTION III

SUMMARY OF RESULTS

The experimental program described herein was designed to examine
hydrazine and hydrazine-derivatives as solvents for various electrolytes. In
principle such solvent/solute mixtures could permit a wide range of electro-
chemical reactions which cannot be achieved in aqueous solutions. Hydrazine
azide as an electrochemically active solute was selected because of the high
theoretical oxidation potential for the azide ion. The kinetics of more con-
ventional metal-metal ion couples were also investigated.

The effect of impurities on the electrochemical properties of hydrazine
was investigated using as-received and specially purified samples. A purifi-
cation procedure was developed which consisted of drying over CaH_2 followed
by a vacuum distillation. This procedure resulted in hydrazine with 0.05 per-
cent water and less than 10 ppm CO_2.

Conductivity measurements were used to characterize the effects of water,
carbon dioxide and aniline (the three major impurities in hydrazine) on the
electrochemical properties of hydrazine. Aniline had no effect on conductivity.
The conductivity as a function of water content was found to obey the Onsager
relationship for water concentrations up to 1.0 percent provided the hydrolysis
reaction with hydrazine was taken into account. Above 1.0 percent water ionic
association is evident and the effect of water on the ionic nature of hydra-
zine is minimized. Thus elaborate purification procedures are not necessary
in order to use hydrazine as a solvent.

The effect of carbon dioxide on the conductivity of hydrazine was
complex. It appears that both carbazic acid and ammonium carbonate are
formed. It has been found that exposure of hydrazine to air must be minimized
in order to maintain a carbon dioxide concentration on the order of 10 ppm.
Proper control of the impurity levels resulted in hydrazine samples that could
be used in electrode polarization studies without encountering interferring
reactions.

Electrode polarization studies on platinum in hydrazine indicated a
total potential range of about 1.2 volts without hydrazine decomposition. The
cathodic reaction is diffusion controlled and proceeds according to:

$$2 \, N_2H_5^+ + 2e \rightarrow 2 \, N_2H_4 + H_2$$
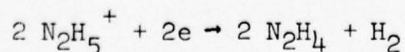
The anodic reaction is activation controlled and proceeds according to:

$$5/2\ N_2H_4 \rightarrow 2\ N_2H_5^+ + 1/2\ N_2 + 2e \ .$$
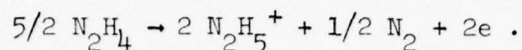
Polarization experiments using hydrazine azide as a solute merely increased the conductivity of the system, there was no evidence of azide ion discharge. These experiments were repeated using monoethylhydrazine as a solvent. The cathodic process was the same as in hydrazine. In the absence of a supporting electrolyte it was possible to obtain a total potential range of $\pm$ 3 volts. In the presence of solutes (including hydrazine azide) the cathodic overpotential was the same as in hydrazine, but there was no evidence of nitrogen evolution at overpotentials as high as + 4 volts (i.e., no azide in activity).

Studies of a variety of metal-metal ion couples in hydrazine indicated that aluminum and magnesium have high overpotentials for solvent decomposition and low overpotentials for the metal-metal salt couple. The aluminum electrode does not appear to be reversible, but the magnesium-magnesium chloride system indicates high reversibility at low overpotentials.

The results suggest that a research program should be conducted in which selected metal-metal ion and metal-insoluble metal salt couples would be investigated as a function of solvent composition and solute concentration in terms of high open-circuit potentials and low overpotentials. The solvent studies have been brought to the point where the solvent-electrode interactions are well understood, and the specific electrode processes can be studied without problems associated with the solvent.

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PUBLICATIONS AND PRESENTATIONS

The significant research results under this contract are being prepared for publication in technical journals or for presentation at technical meetings. The publications include:

1. "The Preparation of Purified Hydrazine", by C. T. Brown. Submitted to The Journal of Chemical and Engineering Data.

2. "The Cathodic Process in Anhydrous Hydrazine", by C. T. Brown. To be submitted to The Journal of the Electrochemical Society.

3. "Electrical Conductivity Studies of Hydrazine-Water, Hydrazine-Aniline and Hydrazine-Carbon Dioxide Mixtures", by C. T. Brown. To be submitted to The Journal of the Electrochemical Society.

A presentation of this work, entitled, "The Electrochemistry of Hydrazine-Hydrazine Azide Mixtures for Battery and Fuel Cell Applications", was made at the University of Poitiers, Poitiers, France, in October, 1974, as part of an International Conference on "The Properties of Hydrazine and its Potential Applications as an Energy Source."

Table I

Purification of Hydrazine

Sample	Percent Water	Notes
N_2H_4 - Stock	2.82	----
N_2H_4 - Stock	2.26	dried over BaO for 24 hrs
N_2H_4 - Stock	0.92	dried over CaH_2 for 30 hrs
N_2H_4 - Stock	0.55	dried over CaH_2 for 51 hrs
N_2H_4 - Stock	0.29	dried over CaH_2 for 75 hrs
N_2H_4 - Stock	0.09	dried over CaH_2 for 231 hrs
N_2H_4 - B	0.69	----
N_2H_4 - B	0.18	dried over CaH_2 for 192 hrs
N_2H_4 - B	0.13	dried over CaH_2 for 231 hrs
N_2H_4 - B	0.11	dried over CaH_2 for 384 hrs
N_2H_4 - B	0.05	dried over CaH_2 for 909 hrs
N_2H_4 - A-1	0.56	----
N_2H_4 - A-1	0.14	vacuum distilled - 1st fraction
N_2H_4 - A-2	1.43	vacuum distilled - 2nd fraction
N_2H_4 - A-2	0.17	vacuum distilled - 1st fraction
N_2H_4 - A-2	0.39	vacuum distilled - 2nd fraction
N_2H_4 - A-2	2.28	vacuum distilled - residue

Table II

Spectrographic Analysis of Metallic Impurities in N_2H_4 After Vacuum Distillation

(Sample A-1)

Sample	Metallic Impurity Level (ppm)		
	Fe	Na	Ni
Original Sample	0.59	0.27	0.08
Distilled Fraction #1	0.31	<0.3	0.06
Distilled Fraction #2	0.66	1.32	0.16
Residue	0.61	0.5	0.05

(Sample A-2)

	Fe	Na	Ni
Fraction #1	0.14	0.34	0.03
Fraction #2	0.27	0.95	0.08
Residue	4.2	2.5	0.58

Table III

Specific Conductivity of Hydrazine as a
Function of Impurity Content

Sample	Specific Conductivity at 25°C (ohm^{-1}-cm^{-1})	Non Volatile Residue (ppm)	H_2O (Percent)	Ash (ppm)	Iron (ppm)	NVR/Ash	Other Major* Impurities (ppm)
1	3.38 x 10^{-5}	3.0	0.76	2.0	0.29	1.5	MMH – 0.085
2	3.94 x 10^{-5}	9.5	1.75	3.6	0.23	2.6	----
3	4.92 x 10^{-5}	12.5	0.95	<1	0.04	>12.5	----
4	5.44 x 10^{-5}	19.4	0.57	1.7	0.59	11.4	MMH – 0.025 Cd – 0.18
5	6.50 x 10^{-5}	13.2	0.64	<1	0.14	>13.2	----

*All samples contain approximately 2 ppm Cl, 0.2 percent Aniline, 0.3 ppm Na and 0.2 percent CO_2.

Table IV

Specific Conductivity of Hydrazine Mixtures
as a Function of Temperature

Sample	Temperature °C	Specific Conductivity ohm^{-1} cm^{-1}
A	24.5	1.709×10^{-4}
A	35.3	1.966×10^{-4}
A	45.2	2.186×10^{-4}
B	25.0	1.012×10^{-4}
B	35.5	1.168×10^{-4}
B	45.2	1.306×10^{-4}
B (384 hrs in CaH$_2$)	25.3	2.279×10^{-5}
B (384 hrs in CaH$_2$)	35.1	2.428×10^{-5}
B (384 hrs in CaH$_2$)	45.3	2.669×10^{-5}

A _____ 1.20% H$_2$O _____ $\Delta E = 2.21 \times 10^3$ cal/mole
B _____ 1.47% H$_2$O _____ $\Delta E = 2.38 \times 10^3$ cal/mole
B (384 hrs in CaH$_2$) ___ 0.11% H$_2$O _____ $\Delta E = 1.56 \times 10^3$ cal/mole

Table V

Conductivity of Hydrazine as a Function of Water Content

H_2O (moles/liter)	Specific Conductivity (ohms^{-1} cm^{-1})	Equivalent Conductivity Λ (ohms^{-1} cm^2)	Degree of Dissociation α	Ionic Concentration αc (moles/liter)	Ionic Equivalent Conductance Λ' (ohms^{-1} cm^2)	%H_2O
7.24×10^{-2}	2.28×10^{-5}	0.3146	3.43×10^{-3}	2.52×10^{-4}	91.7	0.130
1.43×10^{-1}	3.20×10^{-5}	0.2234	2.44×10^{-3}	3.48×10^{-4}	91.5	0.257

Table VI

Conductivity of Hydrazine as a Function of Aniline Content

Aniline (moles/liter)	Specific Conductivity (ohms^{-1} cm^{-1})	Equivalent Conductivity Λ (ohms^{-1} cm^2)	% Aniline
1.03×10^{-2}	4.07×10^{-5}	3.944	0.102
1.93×10^{-2}	4.11×10^{-5}	2.129	0.191
4.23×10^{-2}	4.10×10^{-5}	0.9686	0.419

Table VII

Conductivity of Hydrazine as a Function of Carbon Dioxide Content

CO_2 (moles/liter)	Specific Conductivity (ohms^{-1} cm^{-1})	Equivalent Conductivity Λ (ohms^{-1} cm^2)	$\sqrt{\text{Concentration}}$ (moles/liter)	% CO_2
8.541×10^{-4}	1.3489×10^{-4}	157.932	.0292	.004
1.522×10^{-3}	1.8117×10^{-4}	119.024	.0390	.007
2.002×10^{-3}	2.5019×10^{-4}	124.971	.0447	.009
2.925×10^{-3}	2.6387×10^{-4}	90.209	.0541	.013
4.026×10^{-3}	4.7622×10^{-4}	118.278	.0634	.018
7.296×10^{-3}	9.1079×10^{-4}	124.834	.0854	.032
1.194×10^{-2}	1.0714×10^{-3}	89.735	.1093	.052
1.493×10^{-2}	1.5097×10^{-3}	101.085	.1222	.065
1.879×10^{-2}	1.9102×10^{-3}	101.660	.1371	.082
2.106×10^{-3}	2.5076×10^{-3}	97.686	.1451*	.092*
2.821×10^{-2}	2.8817×10^{-3}	102.151	.1679	.124

* Theoretical weight gain based on 1.81 mg/cc of CO_2

Table VIII

Conductivity of Hydrazine as a Function of Carbon Dioxide Concentration

(In Terms of Ionic Strength for bi-bi and uni-bi Electrolytes)

CO_2 Concentration (moles/liter)	Ionic Strength (J)		$\sqrt{J}$		Specific Conductivity x 10^4	cne (Equivalents/l)	Λ (ohms^{-1} cm^2)
	bi-bi (moles/l)	uni-bi (moles/l)	$\sqrt{\text{bi-bi}}$	$\sqrt{\text{uni-bi}}$			
9.62×10^{-4}	3.85×10^{-3}	2.88×10^{-3}	6.20×10^{-2}	5.36×10^{-2}	1.35	1.92×10^{-3}	70.3
1.38×10^{-3}	5.52×10^{-3}	4.14×10^{-3}	7.44×10^{-2}	6.43×10^{-2}	1.81	2.76×10^{-3}	65.6
2.12×10^{-3}	8.47×10^{-3}	6.36×10^{-3}	9.20×10^{-2}	7.97×10^{-2}	2.64	4.24×10^{-3}	62.4
2.01×10^{-3}	8.04×10^{-3}	6.04×10^{-3}	8.96×10^{-2}	7.77×10^{-2}	2.50	4.02×10^{-3}	62.3
4.26×10^{-3}	1.71×10^{-2}	1.28×10^{-2}	1.31×10^{-1}	1.13×10^{-1}	4.76	8.53×10^{-3}	55.9
8.66×10^{-3}	3.46×10^{-2}	2.60×10^{-2}	1.86×10^{-1}	1.61×10^{-1}	9.10	1.73×10^{-2}	52.6
9.90×10^{-3}	3.96×10^{-2}	2.97×10^{-2}	1.99×10^{-1}	1.72×10^{-1}	10.71	1.98×10^{-2}	54.2
1.48×10^{-2}	5.92×10^{-2}	4.44×10^{-2}	2.44×10^{-1}	2.11×10^{-1}	15.10	2.96×10^{-2}	51.0
2.00×10^{-2}	8.00×10^{-2}	6.00×10^{-2}	2.83×10^{-1}	2.45×10^{-1}	19.10	4.00×10^{-2}	47.7
2.10×10^{-2}	8.40×10^{-2}	6.30×10^{-2}	2.90×10^{-1}	2.51×10^{-1}	20.58	4.20×10^{-2}	48.9
3.30×10^{-2}	1.32×10^{-1}	9.90×10^{-2}	3.64×10^{-1}	3.14×10^{-1}	28.82	6.60×10^{-2}	43.7

Table IX

Anodic Current on a Platinum Electrode as a Function of
Electrolyte and Applied Overpotential

Electrolyte	Applied Overpotential (volts)	Current at Applied Overpotential (milliamps)
N_2H_4 – 1.42% H_2O	1.0	2.5
N_2H_4 – 0.05% H_2O	1.0	0.3
N_2H_4 – 0.05% H_2O	2.5	0.9
N_2H_4 – 0.05% H_2O + Metallic Ions	1.0	2.0
N_2H_4 – 0.05% H_2O + 0.23% N_5H_5	1.0	60

Table X

Anodic Current Density on Platinum as a Function
of Electrolyte Composition

(at a constant overpotential of +0.8v)

Electrolyte*	Anodic Current Density (ma/cm^2)
N_2H_4-A (0.51% H_2O)	1.8
N_2H_4-B (0.13% H_2O)	0.3
N_2H_4-A + 0.19% KCl	35.5
N_2H_4-B + 0.24% KCl	14.0
N_2H_4-B + 0.27% N_5H_5	14.6
N_2H_4-B + 0.23% N_2H_5Cl	14.6

*N_2H_4 A is stock hydrazine containing 0.51% water.

N_2H_4 B is purified hydrazine containing 0.13% water.

Table XI

Cathodic Polarization Peak Currents and
Potentials as a Function of Sweep Rate
(N_2H_4 + 1.43% H_2O)

Peak Current (ma)	Peak Cathodic Over-voltage (volts)	Sweep Rate Milli-volts/sec
0.13	-0.35	6.7
0.25	-0.40	20.0
0.30	-0.48	33.0
0.50	-0.52	46.5
0.75	-0.65	133
0.75	-0.75	200

Table XII
Limiting Cathodic Current as a Function of Electrode Rotation Rate

Sample	Rotation Rate (RPM)	I_ℓ (ma)	$\sqrt{\text{Rate}}$	$I_\ell / \sqrt{\text{Rate}}$
A	81	2.0	9.00	2.22×10^{-1}
	143	3.4	11.9	2.86×10^{-1}
	450	6.0	21.2	2.83×10^{-1}
	960	9.0	31.0	2.90×10^{-1}
B	140	0.090	11.8	7.63×10^{-3}
	360	0.15	19.0	7.90×10^{-3}
	500	0.18	22.4	8.05×10^{-3}
A + .19% KCl	111	1.3	10.54	1.23×10^{-1}
	250	1.8	15.8	1.14×10^{-1}
	315	2.2	17.75	1.24×10^{-1}
B + .24% KCl	115	0.20	10.7	1.87×10^{-2}
	310	0.30	17.6	1.71×10^{-2}
	509	0.40	22.6	1.77×10^{-2}
B + .27% N_5H_5	83	52	9.10	5.72
	135	65	11.6	5.60
	210	84	14.5	5.80
B + .23% N_2H_5Cl	95	46	9.75	4.72
	210	70	14.5	4.73

Table XIII

Diffusion Coefficients for Hydrazonium Ion in Hydrazine

Electrolyte*	I_ϱ(ma)	Measured Concentrations C^O (moles/l)	D(moles/cm^2-sec)	Calculated Concentrations Diffusion Analysis (moles/l)	Hydrolysis Analysis (moles/l)
N_2H_4-B + N_5H_5	84	3.62×10^{-2}	1.67×10^{-5}	--	--
N_2H_4-B + N_2H_5Cl	70	3.38×10^{-2}	1.49×10^{-5}	--	--
N_2H_4-B + KCl	0.4	--	**1.58×10^{-5}	1.82×10^{-4}	2.47×10^{-4}
N_2H_4-A + KCl	2.2	--	**1.58×10^{-5}	1.00×10^{-3}	5.30×10^{-4}

*N_2H_4-A is stock hydrazine containing 0.51% water.

N_2H_4-B is purified hydrazine containing 0.13% water.

** Average value for D based on N_2H_5Cl and N_5H_5 concentrations.

Table XIV

Electrolysis of Hydrazine-Hydrazine Azide Solutions

Run #	Time (Hrs)	# Moles of Gas Per Hour Anode	# Moles of Gas Per Hour Cathode	Total # Moles Initial to End Noted Hr Anode	Total # Moles Initial to End Noted Hr Cathode	Total # Coulombs	# Moles Per Coulomb Anode (Theoretical) 2.5907 x 10⁻⁶ (Experimental)	# Moles Per Coulomb Cathode (Theoretical) 5.1813 x 10⁻⁶	Mole Ratio (H_2/N_2)
1 a		$N_2H_4 + 5.38 \times 10^{-2}$ moles/l N_5H_5							
	1	5.15254×10^{-5}	7.40463×10^{-5}	5.15254×10^{-5}	7.40463×10^{-5}	10.81	4.7665×10^{-6}	6.8498×10^{-6}	1.44
	2	2.89768×10^{-5}	4.36367×10^{-5}	8.96022×10^{-5}	1.176830×10^{-4}	20.62	3.7281×10^{-6}	5.4432×10^{-6}	1.46
	3	2.45759×10^{-5}	5.21539×10^{-5}	1.051781×10^{-4}	1.698369×10^{-4}	32.43	3.2432×10^{-6}	5.2370×10^{-6}	1.61
	4	1.53357×10^{-5}	6.07156×10^{-5}	1.205138×10^{-4}	2.305525×10^{-4}	43.37	2.7787×10^{-6}	5.3159×10^{-6}	1.91
	5	2.37469×10^{-5}	5.28479×10^{-5}	1.442607×10^{-4}	2.834004×10^{-4}	54.18	2.6626×10^{-6}	5.2307×10^{-6}	1.96
1 b		$N_2H_4 + 5.83 \times 10^{-2}$ moles/l N_5H_5							
	1	1.82673×10^{-5}	2.66666×10^{-5}	1.82673×10^{-5}	2.66666×10^{-5}	10.81	1.6899×10^{-6}	2.4668×10^{-6}	1.46
	2	2.52059×10^{-5}	4.69831×10^{-5}	4.36732×10^{-5}	7.36497×10^{-5}	21.62	2.0108×10^{-6}	3.4066×10^{-6}	1.69
	3	1.23821×10^{-5}	6.04122×10^{-5}	5.5853×10^{-5}	1.340619×10^{-4}	32.43	1.7223×10^{-6}	4.1339×10^{-6}	2.40
	4	2.00029×10^{-5}	5.70852×10^{-5}	7.58582×10^{-5}	1.911471×10^{-4}	43.24	1.7544×10^{-6}	4.4206×10^{-6}	2.52
	5	2.791×10^{-5}	4.80522×10^{-5}	1.037782×10^{-4}	2.391993×10^{-4}	54.2	1.9147×10^{-6}	4.4133×10^{-6}	2.30
2		$N_2H_4 + 5.38 \times 10^{-2}$ moles/l N_5H_5 + 0.617 moles/l H_2O							
	1	3.72576×10^{-5}	4.78014×10^{-5}	3.72576×10^{-5}	4.78014×10^{-5}	10.81	3.4466×10^{-6}	4.4220×10^{-6}	1.28
	2	2.96116×10^{-5}	7.01361×10^{-5}	6.58692×10^{-5}	1.179375×10^{-4}	20.61	3.0481×10^{-6}	5.4575×10^{-6}	1.79
	3	2.52269×10^{-5}	5.26165×10^{-5}	9.10961×10^{-5}	1.705540×10^{-4}	32.42	2.8099×10^{-6}	5.2608×10^{-6}	1.87
	4	1.74925×10^{-5}	3.64726×10^{-5}	1.085896×10^{-4}	2.070267×10^{-4}	43.23	2.5119×10^{-6}	4.7890×10^{-6}	1.91
	5	1.01731×10^{-5}	4.52101×10^{-5}	1.187617×10^{-4}	2.522358×10^{-4}	54.10	2.1952×10^{-6}	4.6624×10^{-6}	2.12
3		$N_2H_4 + 3.72 \times 10^{-2}$ moles/l N_5H_5 + 4.15×10^{-1} moles/l H_2O							
	1	5.32015×10^{-5}	5.79886×10^{-5}	5.32015×10^{-5}	5.79886×10^{-5}	10.81	4.9215×10^{-6}	5.3643×10^{-6}	1.09
	2	3.16002×10^{-5}	5.25162×10^{-5}	8.48017×10^{-5}	1.105048×10^{-4}	21.61	3.9242×10^{-6}	5.1136×10^{-6}	1.30
	3	2.27136×10^{-5}	5.87848×10^{-5}	1.075153×10^{-4}	1.692896×10^{-4}	32.42	3.3163×10^{-6}	5.2218×10^{-6}	1.43
	4	2.18895×10^{-5}	5.35853×10^{-5}	1.294048×10^{-4}	2.228749×10^{-4}	43.23	2.9934×10^{-6}	5.1556×10^{-6}	1.72
	5	3.10197×10^{-5}	5.12150×10^{-5}	1.604245×10^{-4}	2.740899×10^{-4}	54.04	2.9686×10^{-6}	5.0720×10^{-6}	1.71

Table XV

Physical Properties of Water, Hydrazine,
Monomethyl Hydrazine and Unsymmetrical
Dimethyl Hydrazine

Physical Property	H_2O	N_2H_4	MMH	UDMH
Melting Point (°C)	0	1.53	-52	-57
Normal Boiling Point (°C)	100	114	88	62
Vapor Pressure (298°K) (mmH_g)	23.7	14.2	49	167
Density (298°K) (g/cc)	0.997	1.004	0.87	0.79
Viscosity (298°K) (centipoise)	0.894	0.913	0.775	0.492
Surface Tension (298°K) (dynes/cm)	72	66	34	24
Dielectric Constant (298°K)	80	52	19	-

Table XVI

Cell Potentials for Electrode Couples in Hydrazine

Cell #	Metal 1	Couple	2	1.7 Molar NaN$_3$ Potential (V)	Half cell Potential (V) Metal 1-Ref	Metal 2-Ref
1	Al	-	Mg	1.44	-.06	-1.50
2	Al	-	Pb	1.22	-0.68	+0.54
3	Al	-	Ni	0.28	-0.10	+0.18
*4	Mg	-	Pb	1.68	-1.35	+0.33
*5	Al	-	Pb	0	+0.30	+0.31
6**	Mg	-	Pb	1.71	-1.48	+0.23
7**	Mg	-	Ni	1.52	-1.45	+0.08

1.3 Molar NaNO$_3$

8	Al	-	Mg	0.60	-0.18	-0.80
9	Al	-	Pb	0.46	-0.28	+0.22
10	Al	-	Ni	0.14	-0.11	+0.03
11	Mg	-	Ni	0.52	-0.62	-0.10
*12	Al	-	Ni	1.00	-0.93	+0.07
*13	Al	-	Pb	1.18	-0.85	+0.33

5.3 Molar H$_2$O - 1.1 Molar NaOH

14	Al	-	Mg	0.80	-1.04	-0.14
15	Ni	-	Mg	0.15	+0.07	-0.06
16	Pb	-	Mg	0.35	+0.25	-0.11
*17	Al	-	Mg	1.06	-0.95	+0.11
*18	Pb	-	Mg	0.35	+0.25	-0.11
*19	Al	-	Ni	1.10	-0.88	+0.22

*   Electrolysis to produce anodic and cathodic products
** Cell short circuited

Table XVII

Overpotentials for Magnesium, Aluminum, Nickel and Lead

Metal	NaN$_3$			NaNO$_3$			NaOH - H$_2$O		
	Anode	Cathode	Total	Anode	Cathode	Total	Anode	Cathode	Total
Al	3.5	0.6	4.1	4.2	1.6	5.8		0.2	0.2
Mg	0.2	0.2	0.4	2.6	0.2	2.8	3.0	1.8	4.8
Ni	1.0	0.6	1.6	1.0	1.0	2.0	1.5	0.4	1.0
Pb	-	-	-	-	-	-	-	-	-

Electrolyte

Table XVIII

Electrode Potentials for Magnesium and Aluminum

In solutions containing NaCl, LiN_3, $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$

Metal	Electrolyte	Potentials Glass
Mg	N_2H_4-NaCl (1.7 molar)	-1.34
"	"	-0.810
		-0.690
Mg	N_2H_4-NaCl-$MgCl_2 \cdot 6H_2O$	-2.20
Mg	N_2H_4-LiN_3 (0.26 molar)	-2.08
"	"	-2.26
Al	N_2H_4-NaCl (1.7 molar)	-1.046
"	N_2H_4-NaCl + $AlCl_3 \cdot 6H_2O$	-0.670

FIG. 1

ANODIC POLARIZATION ON PLATINUM IN N_2H_4–0.05 % H_2O

(ANODIC FILM FORMATION)
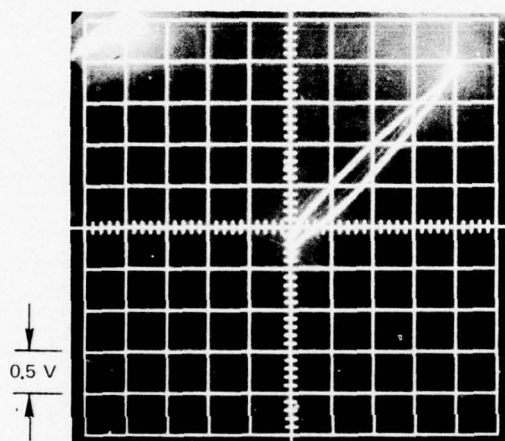
A. FIRST ANODIC SWEEP
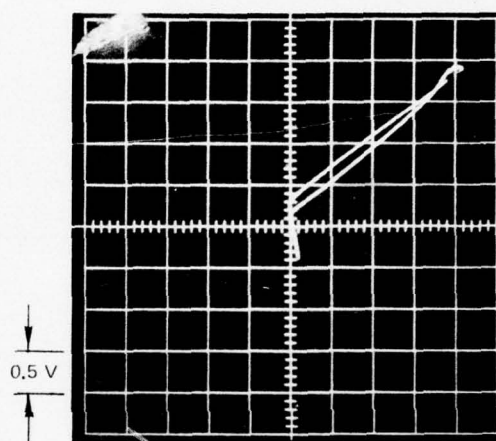
B. SECOND ANODIC SWEEP
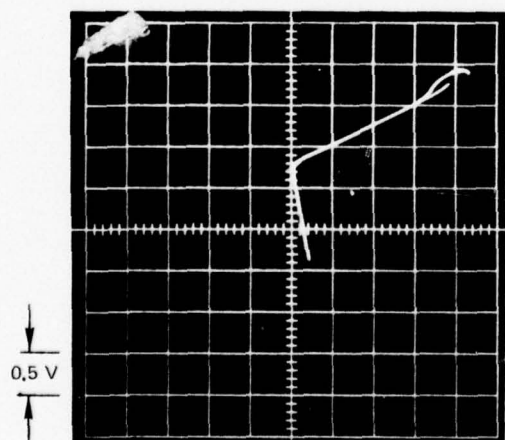
C. EIGHTH ANODIC SWEEP
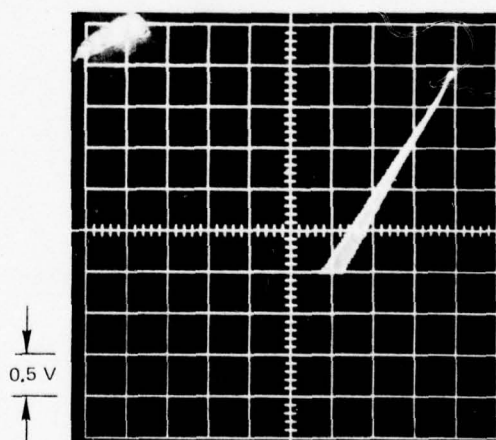
D. NINTH ANODIC SWEEP

FIG. 2

ANODIC POLARIZATION ON PLATINUM IN N_2H_4–0.23% N_5H_5

(EFFECT OF ROTATION)

0.05 V
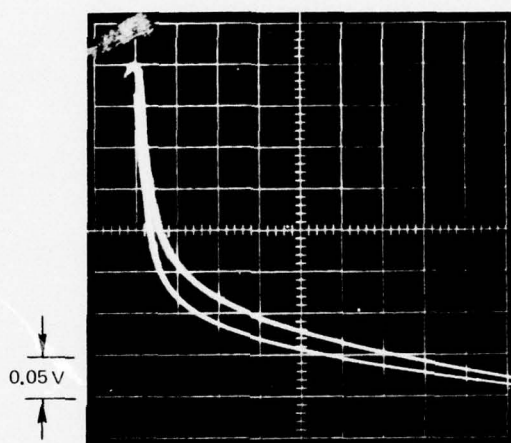
0.5 ma

A. STAGNANT ELECTROLYTE
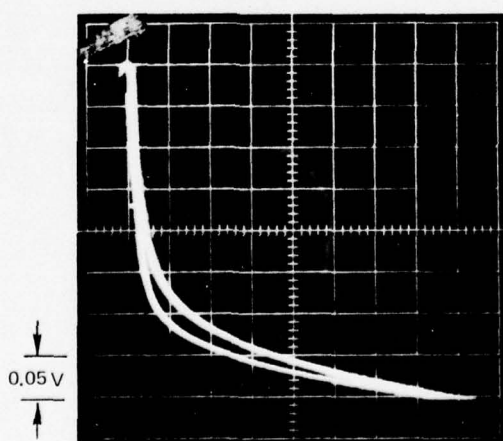
0.05 V

0.5 ma

B. ROTATING ELECTRODE (900 rpm)

FIG. 3

ANODIC POLARIZATION ON PLATINUM AS A FUNCTION
OF ELECTROLYTE COMPOSITION

Legend:
- ○ N_2H_4–A
- □ N_2H_4–B
- △ N_2H_4–A + 0.19% KCl
- ▽ N_2H_4–B + 0.24% KCl
- ◇ N_2H_4–B + 0.27% N_5H_5
- ◁ N_2H_4–B + 0.23% N_2H_5 Cl

CURRENT DENSITY (MA/CM^2)

η (VOLTS)

FIG. 4
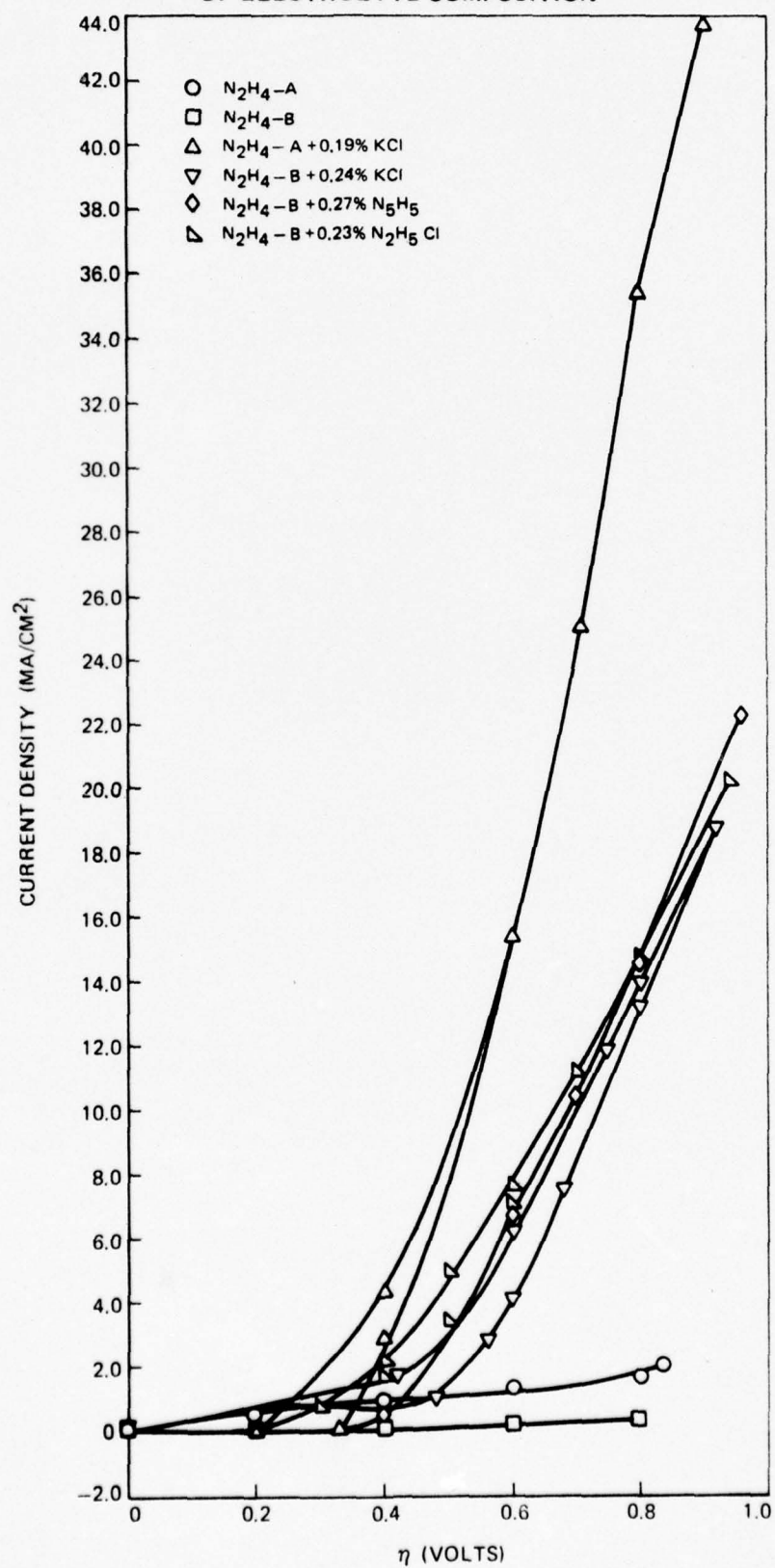
CATHODIC POLARIZATION AS A FUNCTION OF ELECTROLYTE COMPOSITION

0.2 V
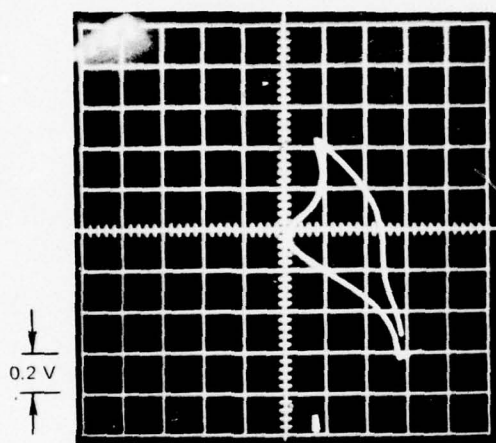
0.25 ma

A. N_2H_4 – 1.43% H_2O

0.2 V

0.2 ma

B. N_2H_4 – METALLIC CONTAMINANTS

0.2 V

0.1 ma

C. N_2H_4 – 0.05% H_2O

0.2 V
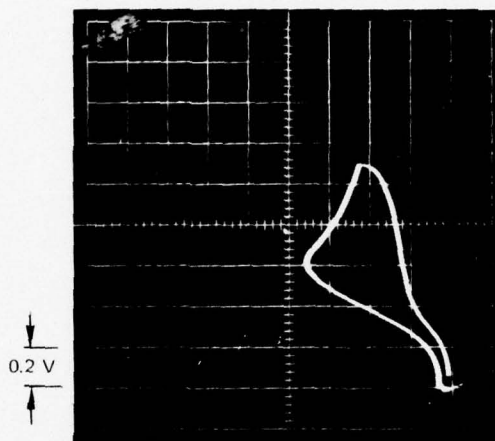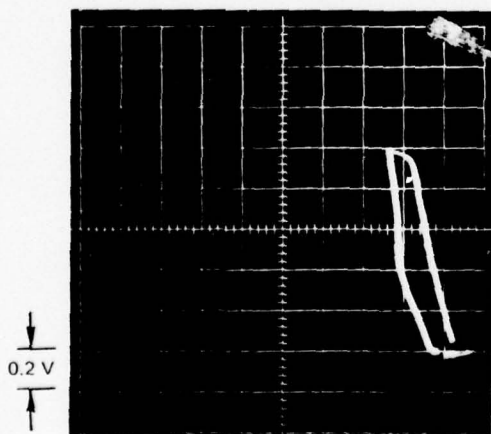
5.0 ma

D. N_2H_4 – 0.23% N_5H_5

FIG. 5

CATHODIC POLARIZATION ON PLATINUM
EFFECT OF ROTATION

0.2 V

0.2 ma
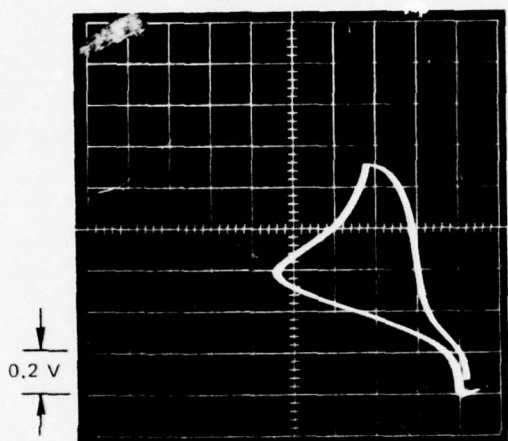
A. N_2H_4 – METALLIC CONTAMINANTS

0.2 V

0.2 ma
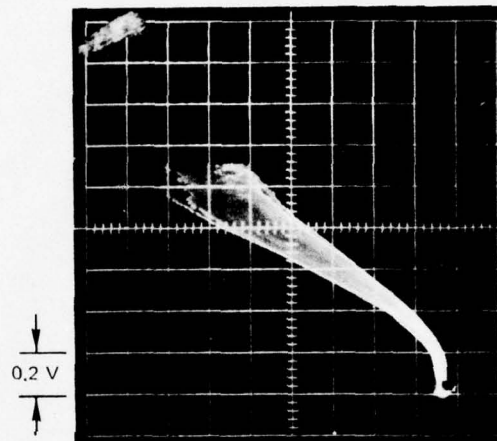
B. N_2H_4 – METALLIC CONTAMINANTS
ROTATING ELECTRODE (900 rpm)

0.5 V

0.5 ma

C. N_2H_4 – 0.05% H_2O

0.5 V

0.5 ma
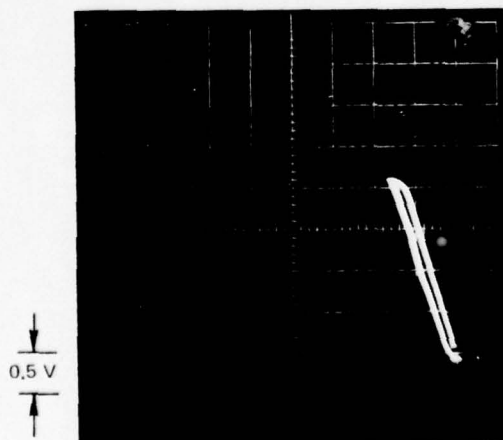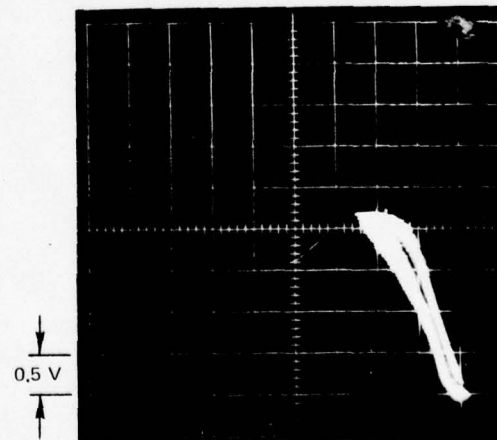
D. N_2H_4 – 0.05% H_2O

ROTATING ELECTRODE (900 rpm)

CATHODIC LIMITING CURRENT AS A FUNCTION OF ROTATION RATE

$(N_2H_4 - 0.23\% N_5H_5)$

0.2 V

20.0 ma.
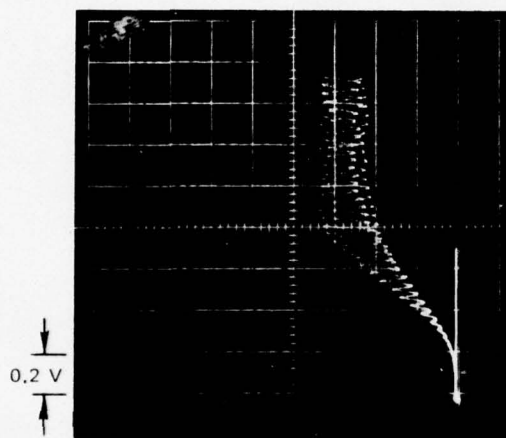
A. ROTATION AT 210 rpm

0.2 V

20.0 ma
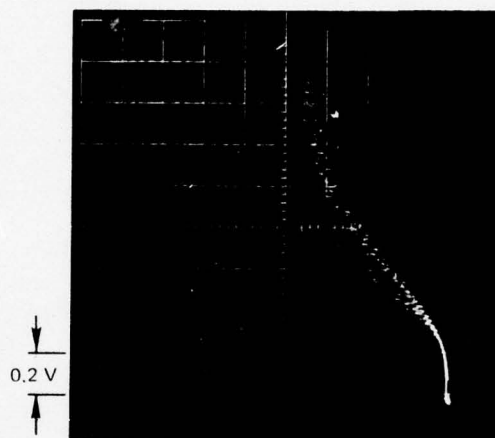
B. ROTATION AT 400 rpm

0.2 V

20.0 ma
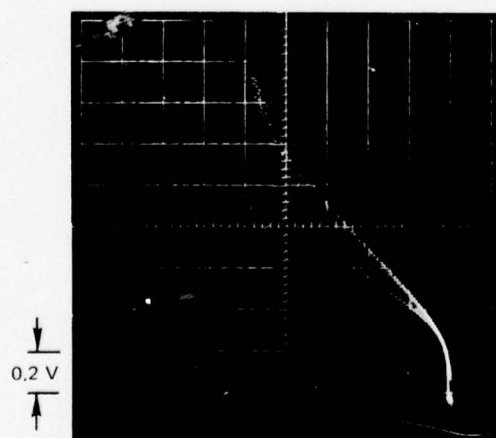
C. ROTATION AT 510 rpm

FIG. 7

CATHODIC POLARIZATION ON PLATINUM AS A FUNCTION OF ELECTROLYTE COMPOSITION
(EFFECT OF KCl AND H$_2$O)

O N$_2$H$_4$ – A

□ N$_2$H$_4$ – B

△ N$_2$H$_4$ – A + 0.19% KCl

✕ N$_2$H$_4$ – B + 0.24% KCl

CURRENT DENSITY (MA/CM^2)

η (VOLTS)

FIG. 8
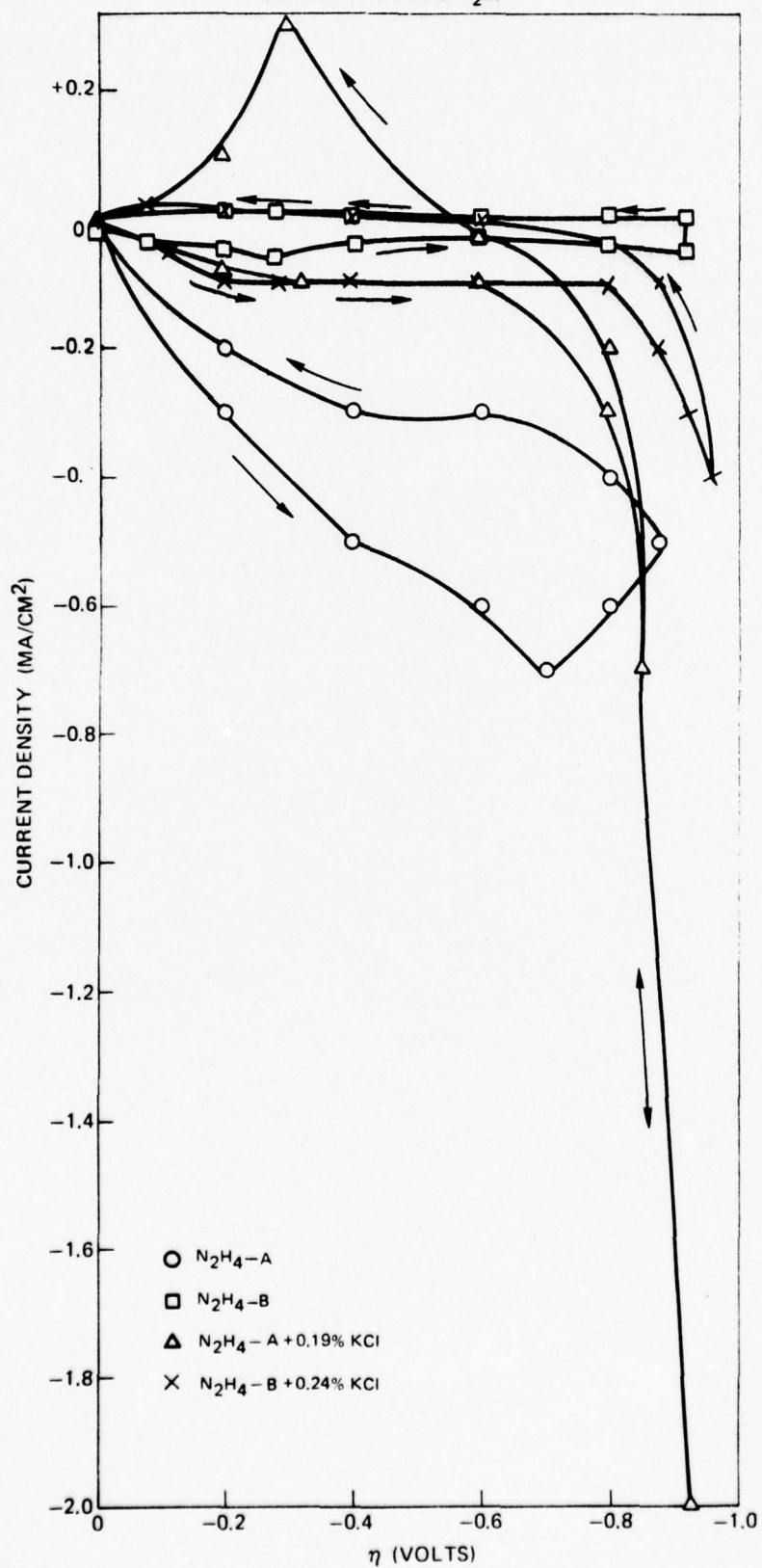
CATHODIC POLARIZATION ON PLATINUM IN N_2H_4–0.19% KCl–0.61% H_2O
AS A FUNCTION OF SURFACE COVERAGE

FIG. 9
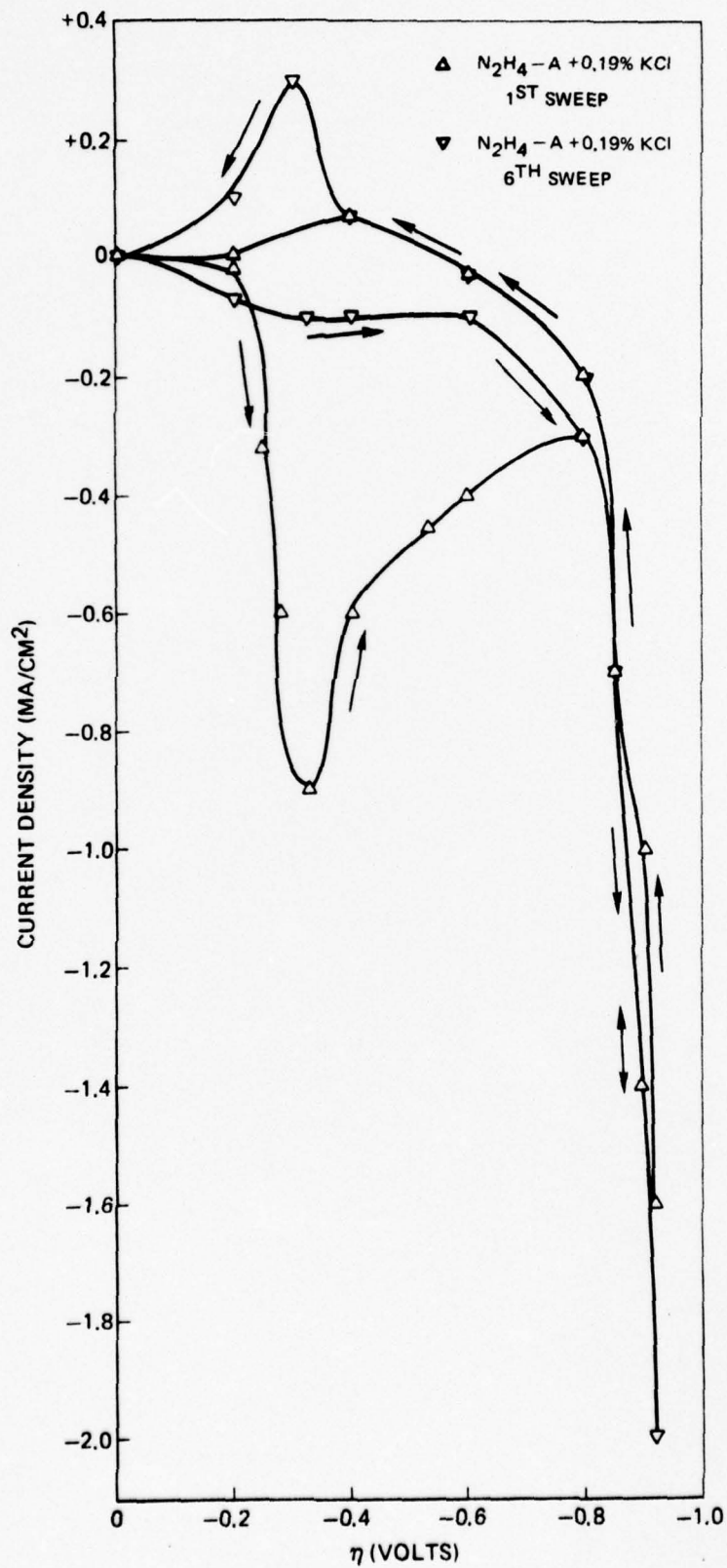
CATHODIC POLARIZATION ON PLATINUM IN N_2H_4—0.24% KCl — 0.13% H_2O
AS A FUNCTION OF SURFACE COVERAGE

FIG. 10
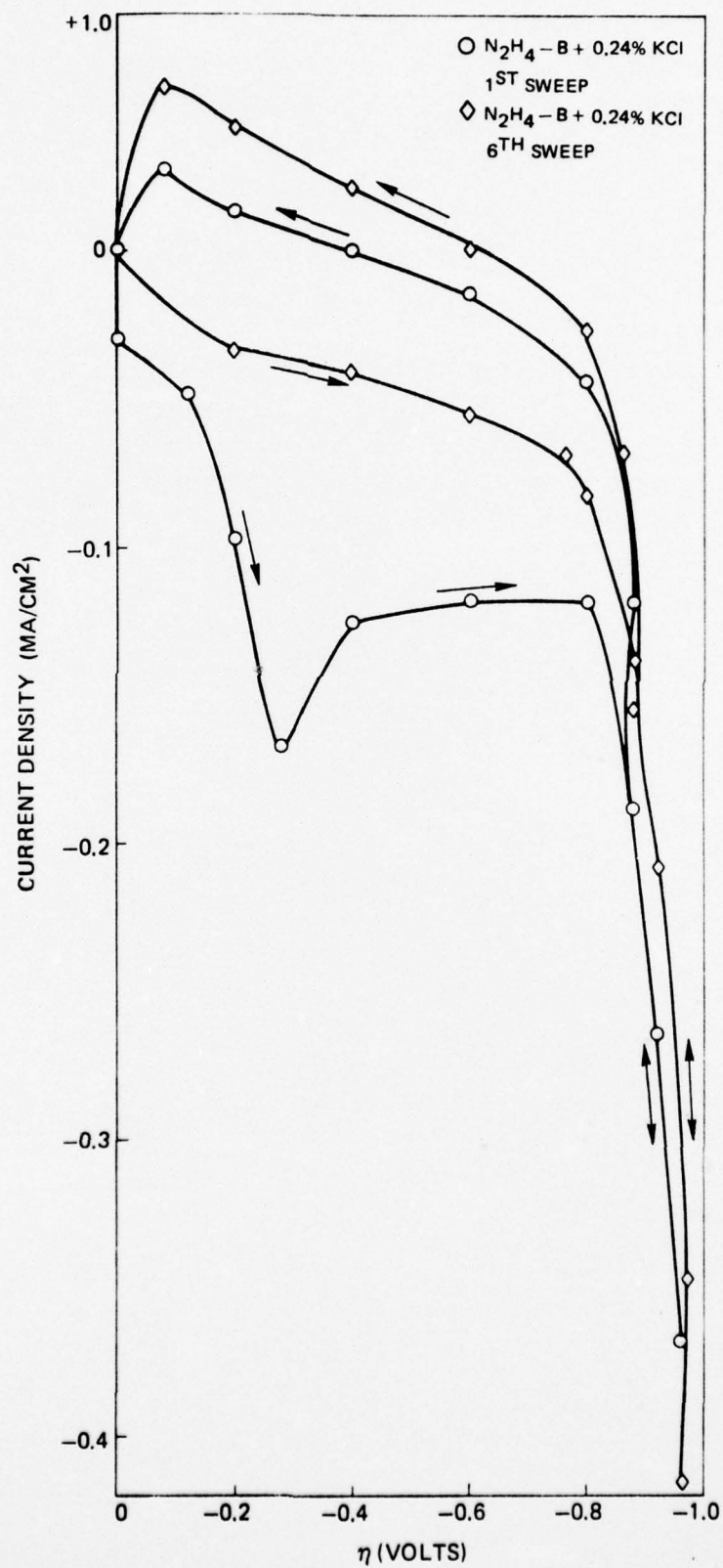
CATHODIC POLARIZATION ON PLATINUM IN N_2H_4 + 0.51% H_2O
(EFFECT OF POTENTIAL SCAN RATE)

△ $N_2H_4 - A_1$ (200 MV/SEC)

□ $N_2H_4 - A_2$ (20 MV/SEC)

○ $N_2H_4 - A_3$ (6.7 MV/SEC)

CURRENT DENSITY (MA/CM^2)

0

−0.2

−0.4

−0.6

−0.8

η (VOLTS)

0   −0.2   −0.4   −0.6   −0.8   −1.0   −1.2

FIG. 11
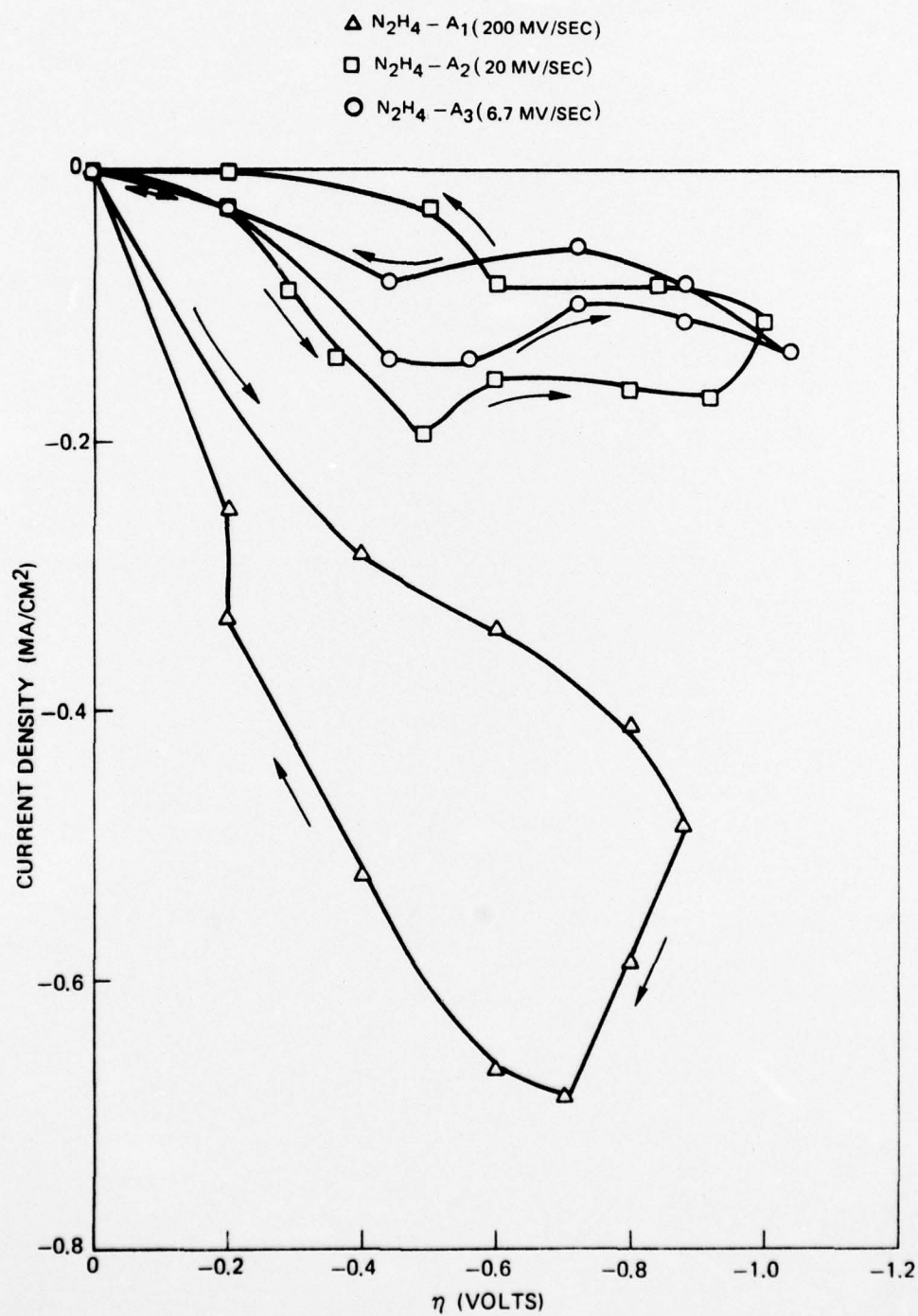
CATHODIC POLARIZATION ON PLATINUM AS A FUNCTION OF ELECTROLYTE COMPOSITION

(EFFECT OF N_5H_5 AND N_2H_5Cl IN N_2H_4 + 0.13% H_2O)
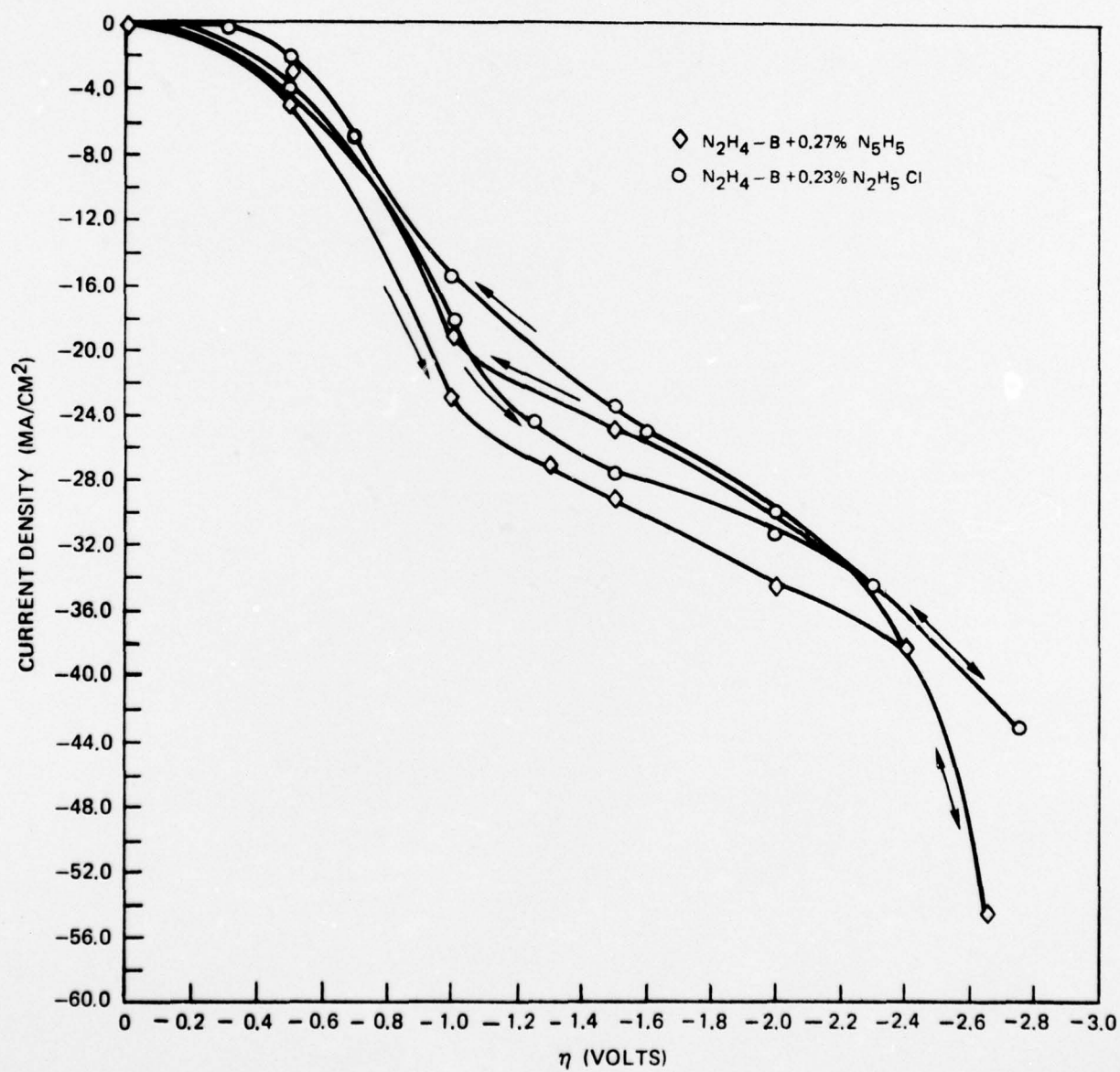
Legend:
◇ $N_2H_4 - B + 0.27\%$ N_5H_5
○ $N_2H_4 - B + 0.23\%$ N_2H_5 Cl

Y-axis: CURRENT DENSITY (MA/CM^2)
X-axis: η (VOLTS)

FIG. 12

CATHODIC POLARIZATION ON PLATINUM AS A FUNCTION OF ELECTROLYTE COMPOSITION

(EFFECT OF ROTATION FOR KCl IN N_2H_4 + 0.61% H_2O)

FIG. 13
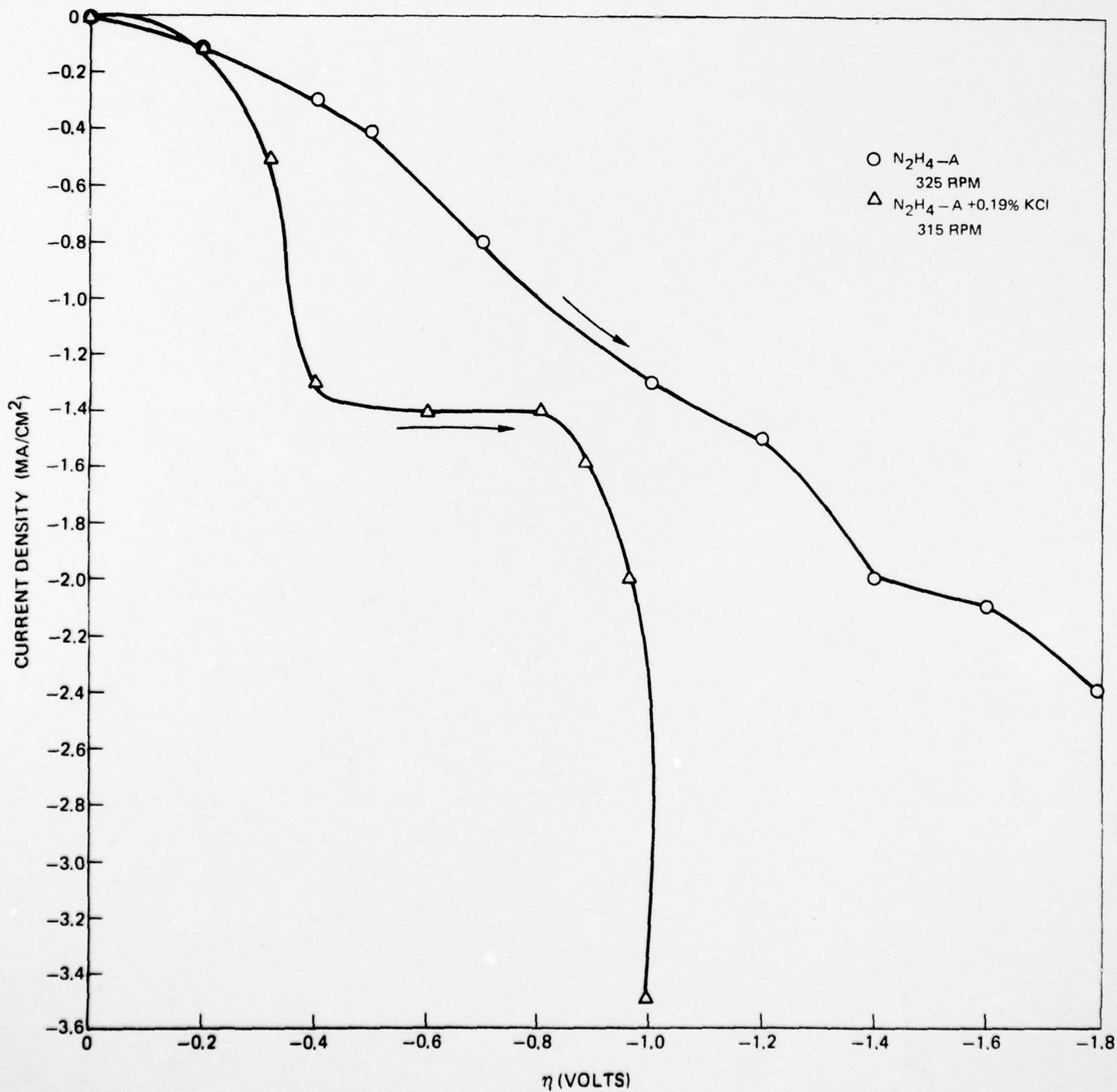
CATHODIC POLARIZATION ON PLATINUM AS A FUNCTION OF ELECTROLYTE COMPOSITION

(EFFECT OF ROTATION FOR KCl IN N_2H_4 + 0.13% H_2O)
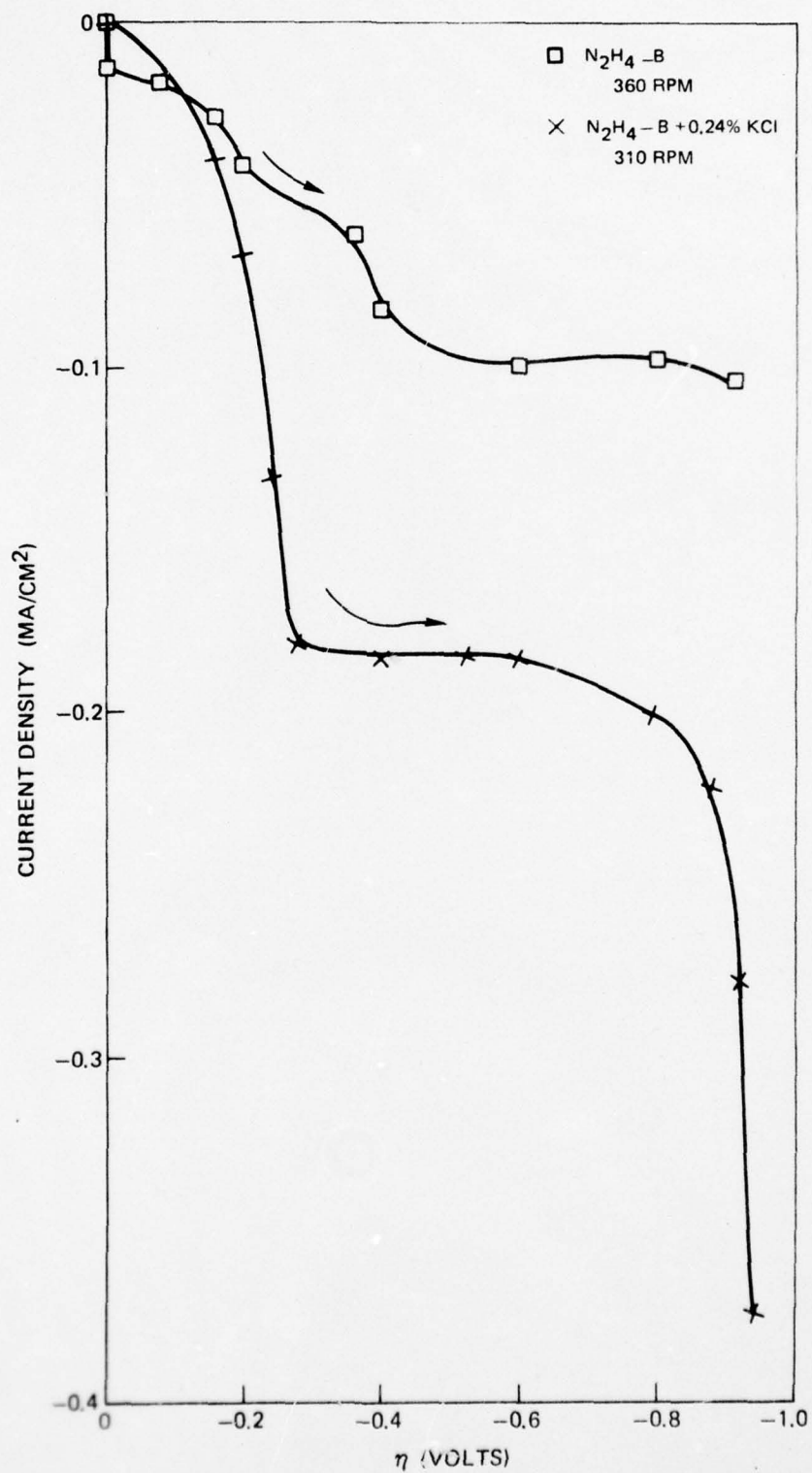
FIG. 14

CATHODIC POLARIZATION ON PLATINUM AS A FUNCTION OF
ELECTROLYTE COMPOSITION

(EFFECT OF ROTATION FOR N_5H_5 AND N_2H_5Cl IN N_2H_4 + 0.13% H_2O)
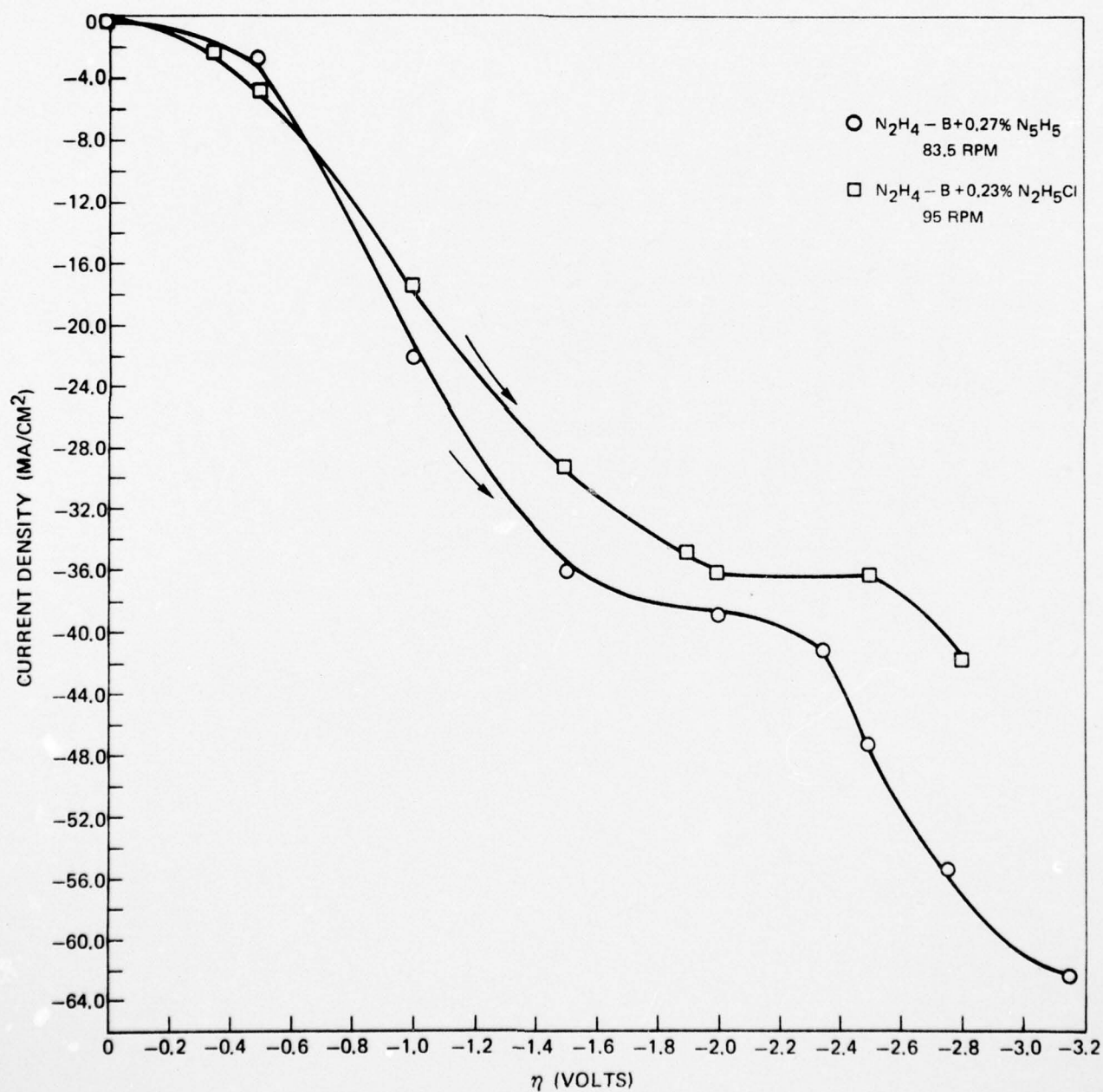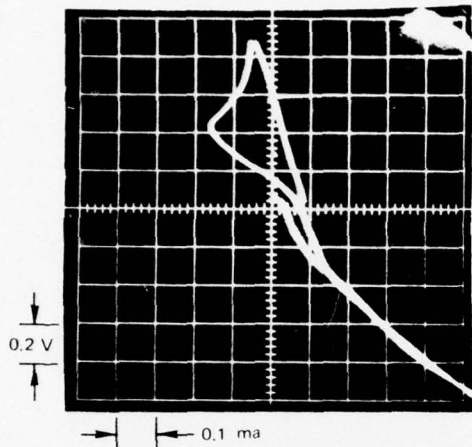
ANODE – CATHODE INTERACTIONS
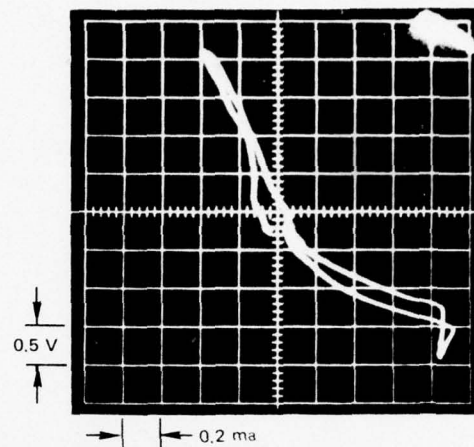
FIG. 15

0.2 V

0.1 ma

A. N_2H_4 – 0.05% H_2O
POLARIZATION INITIALLY ANODIC

0.5 V

0.2 ma

B. N_2H_4 – 0.05% H_2O
POLARIZATION INITIALLY CATHODIC

0.2 V

0.5 ma

C. N_2H_4 – METALLIC CONTAMINANTS
POLARIZATION INITIALLY ANODIC

0.2 V

0.5 ma

D. N_2H_4 – METALLIC CONTAMINANTS
POLARIZATION INITIALLY CATHODIC

0.2 V

20.0 ma
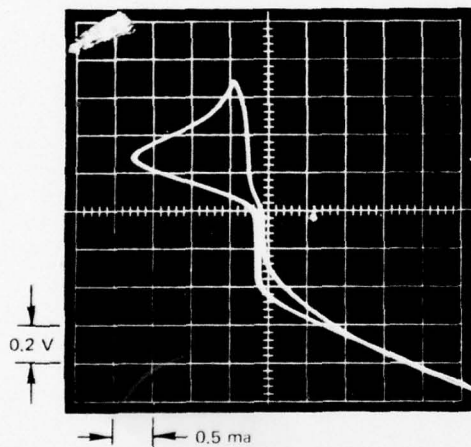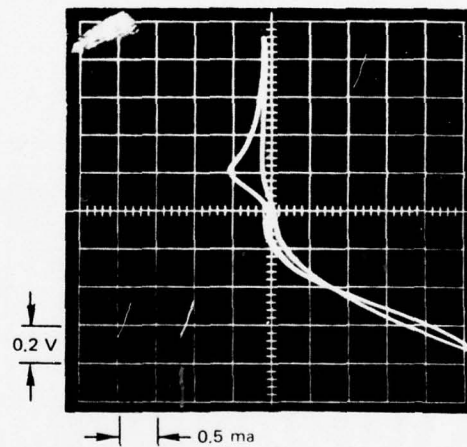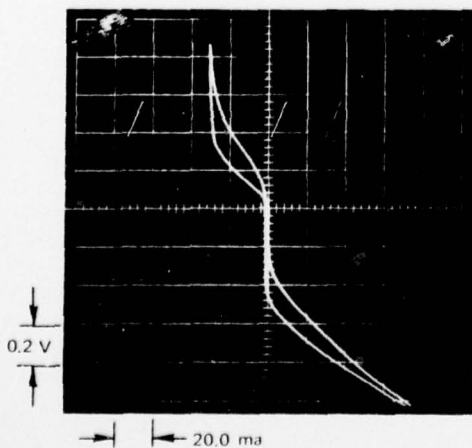
E. N_2H_4 – 0.23% N_5H_5
POLARIZATION INITIALLY ANODIC

0.2 V

20.0 ma
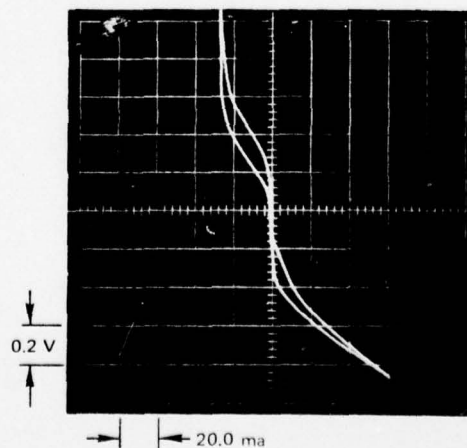
F. N_2H_4 – 0.23% N_5H_5
POLARIZATION INITIALLY CATHODIC

FIG. 16

ELECTROCHEMICAL REACTIONS

FOR 23% HYDRAZINE AZIDE-77% HYDRAZINE

ANODIC REACTIONS

	ΔF°_{ox} (KCAL/MOLE)	E° (VOLTS)	E VS SCE* (VOLTS)
1. $2N_3^- \rightleftarrows 3N_2 + 2e$	-155.4	-3.34	-3.82
2a. $1/2\ N_2H_4 + 2OH^- \rightleftarrows 1/2\ N_2 + 2H_2O + 2e$ $2N_2H_4 + 2H_2O \rightleftarrows 2N_2H_5^+ + 2OH^-$	-56.0	-1.21	-1.39
2b. $5/2\ N_2H_4 \rightleftarrows 1/2\ N_2 + 2N_2H_5^+ + 2e$	-47.1	-1.02	-1.39

CATHODIC REACTIONS

	ΔF°_{red} (KCAL/MOLE)	E° (VOLTS)	E VS SCE (VOLTS)
1a. $2N_2H_5^+ + 2e \rightleftarrows H_2 + 2N_2H_4$ $2N_2H_4 + 2H_2O \rightleftarrows 2N_2H_5^+ + 2OH^-$	+29.4	-0.64	-0.81
1b. $2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	+38.2	-0.83	-0.81
2. $2N_2H_5^+ + 2e \rightleftarrows 2NH_3 + N_2H_4$	-14.3	+0.31	+0.01
3. $2N_2H_5^+ + 2e \rightleftarrows 2NH_3 + 2H_2 + N_2$	-50.0	+1.08	+1.44

*SCE is Saturated Calomel Electrode

FIG. 17

POLARIZATION ON PLATINUM FOR HYDRAZINE AND MONOMETHYL HYDRAZINE

△ N_2H_4
□ $CH_3N_2H_3$
○ $CH_3N_2H_3$ + KCl

FIG. 18
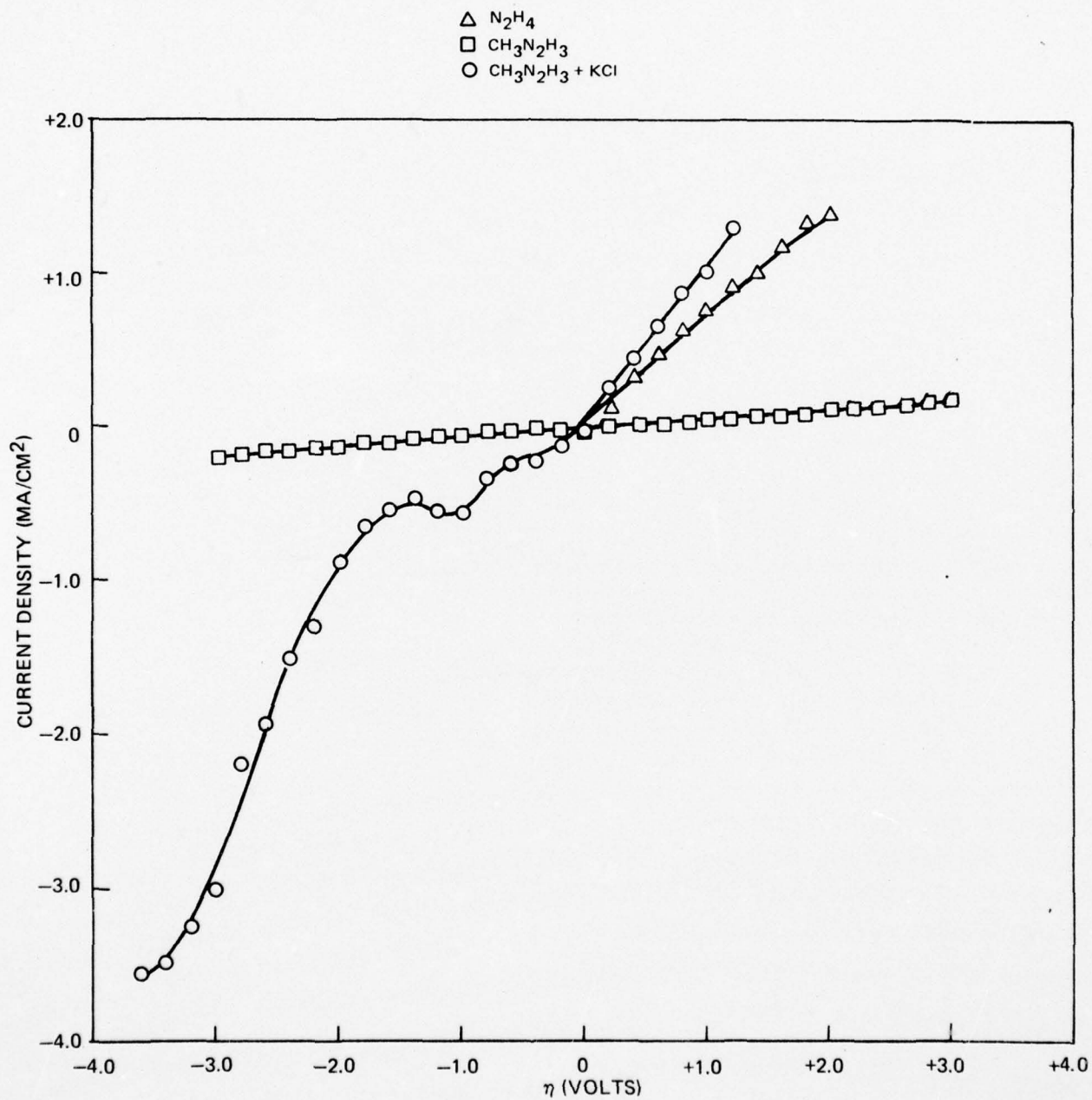
CURRENT–VOLTAGE RELATIONSHIP IN N_2H_4

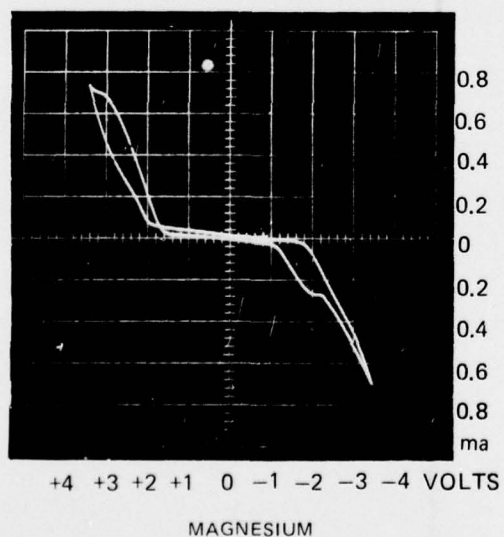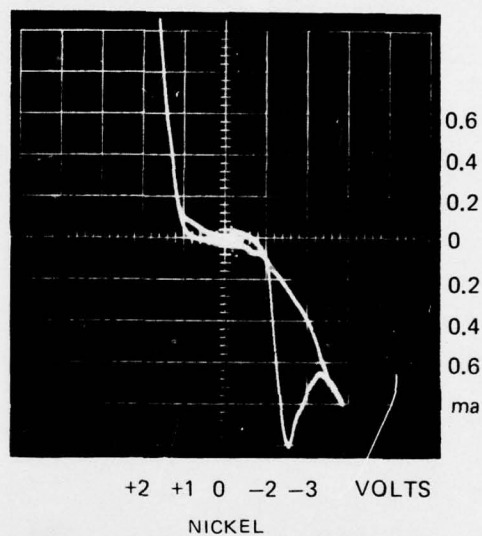## (1.7 MOLAR NaN_3)
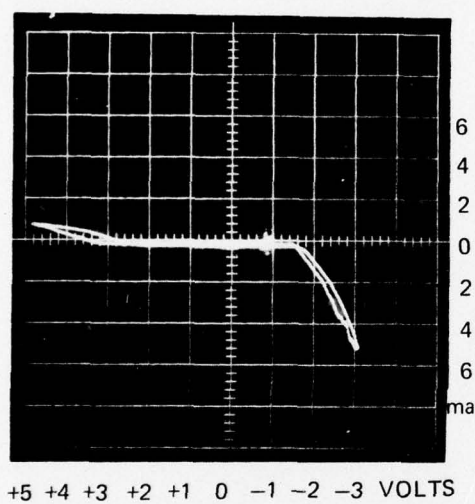
ALUMINUM
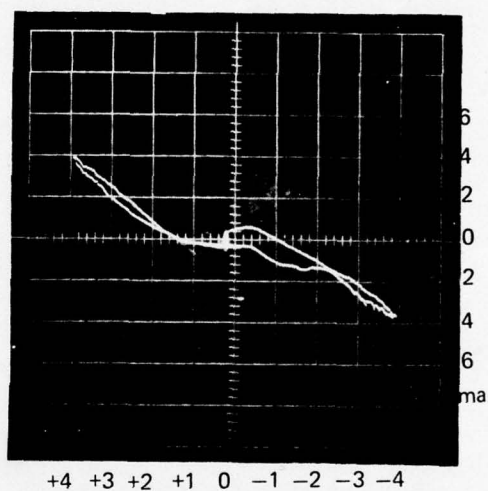
NICKEL
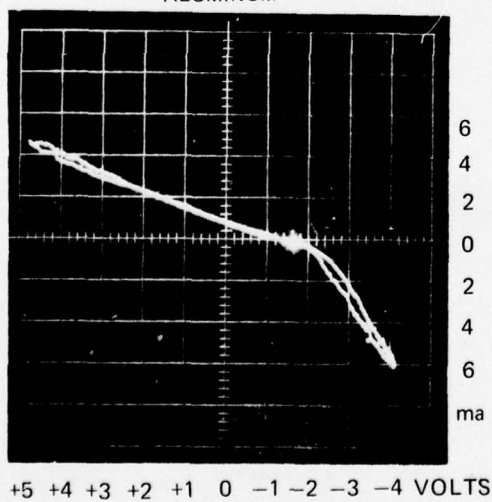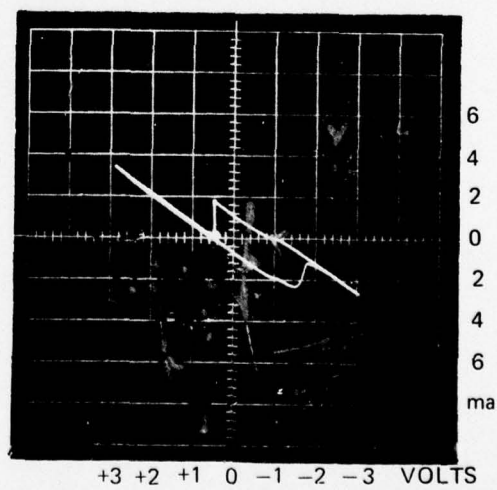
MAGNESIUM

LEAD

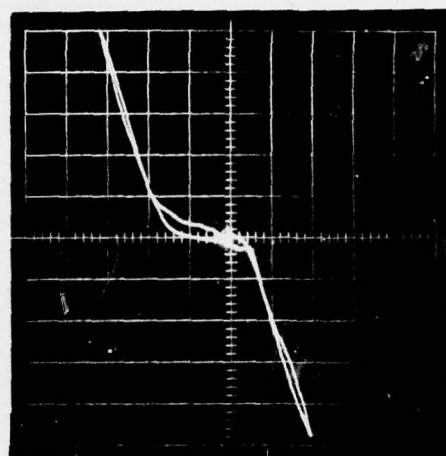# CURRENT–VOLTAGE RELATIONSHIP IN N_2H_4

(1.3 MOLAR $NaNO_3$)

ALUMINUM

NICKEL

MAGNESIUM

LEAD

FIG. 20
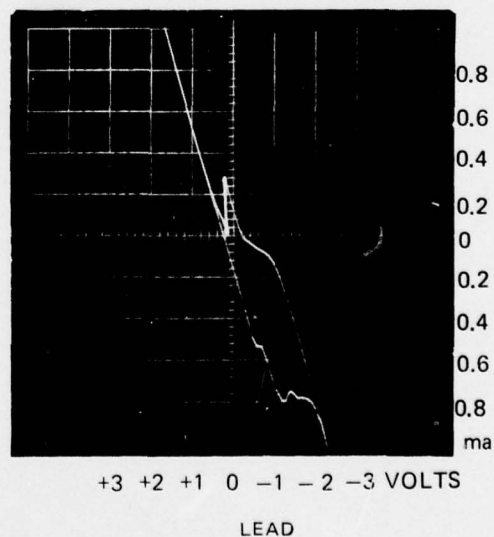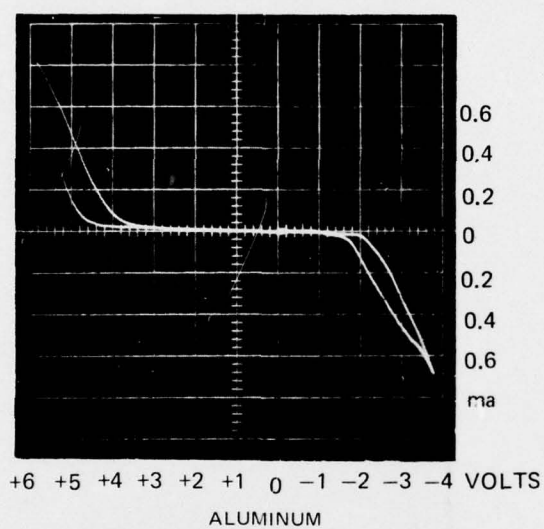
CURRENT–VOLTAGE RELATIONSHIP IN N_2H_4

(5.3 MOLAR H_2O–1.1 MOLAR NaOH)
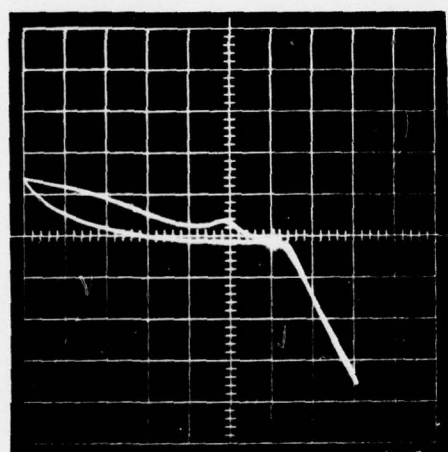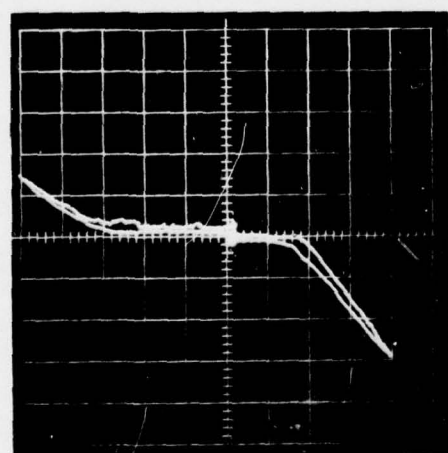
ALUMINUM

NICKEL

MAGNESIUM

LEAD

76-09-99-1
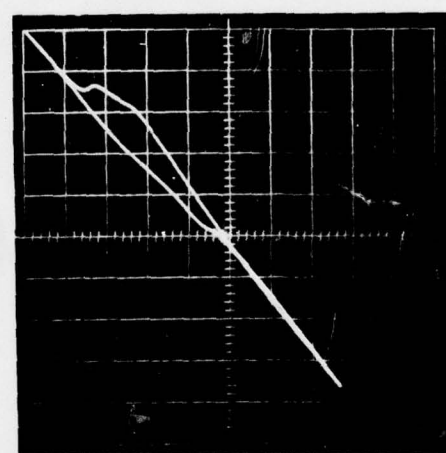
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	6. PERFORMING ORG. REPORT NUMBER

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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Hydrazine Azide

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This document constitutes the final report under Contract F44620-72-C-0049, "Electrochemistry of Hydrazine-Hydrazine Azide Mixtures". The final report contains a summary of the research accomplished for the period, March 1, 1972 through June 30, 1976. Investigations into the nature of hydrazine and hydrazine derivatives were carried out with the objective of providing solvents for electrochemical applications which exhibit large potential ranges without

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sacrificing solubility levels of the reactants. The activity of the azide ion was also examined since its theoretical cell potential is high. The experimental investigations included the development of methods for the purification of hydrazine and the determination of the basic electrochemical properties of hydrazine.

The effect of impurities on the conductivity of hydrazine was also determined as a function of water and carbon dioxide content. Electrode polarization measurements on platinum in the presence of hydrazine indicates that the azide ion is not electrochemically active and the electrode processes are due to the solvent itself. The basic cathodic reaction is the reduction of the hydrazonium ion to hydrogen and the anodic reaction is the oxidation of hydrazine to the hydrazonium ion and nitrogen. Studies in monomethylhydrazine and unsymmetrical dimethyhydrazine indicated an improved anodic overpotential (no nitrogen formation); however the cathodic reaction was identical to hydrazine. The program direction was changed to the study of metal-metal ion couples in hydrazine and it was found that the magnesium-magnesium ion couple was reversible and that magnesium and aluminum metals exhibit a high overpotential for solvent decomposition. Thus metal-metal ion and metal-insoluble metal salt couples should be investigated further.